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TITLE OF THESIS: Thermodynamics of Aqueous Solutions

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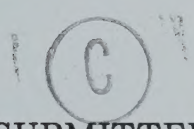
THERMODYNAMICS OF AQUEOUS SOLUTIONS

BY

JAMEY KARL HOVEY



A THESIS

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled *Thermodynamics of Aqueous Solutions* submitted by Jamey Karl Hovey in partial fulfilment of the

Date: October 7, 1988

This thesis is dedicated to my parents Gordon and Shirley who have given me my life, education, and more than I can say. I love them both dearly.

ABSTRACT

Measurements of the densities and heat capacities of aqueous solutions have led to defined apparent molar volumes and heat capacities for many aqueous electrolytes, mostly over the temperature range 10-55°C.

Results are presented for aqueous ions from the systems: aluminum [$Al(OH)_4^-(aq)$ and $Al^{3+}(aq)$], boron [$B(OH)_3$ and $B(OH)_4^-(aq)$], iron [$Fe^{2+}(aq)$ and $Fe^{3+}(aq)$], uranium [$UO_2^{2+}(aq)$, $UO_2Cl^+(aq)$, $UO_2NO_3^+(aq)$, and $UO_2SO_4(aq)$], sulphur [$SO_4^{2-}(aq)$ and $HSO_4^-(aq)$], chromium [$CrO_4^{2-}(aq)$, $HCrO_4^-(aq)$, and $Cr_2O_7^{2-}(aq)$], several species of aqueous ethylenediaminetetraacetic acid (EDTA) and several mono- and divalent chelates, and finally for two important acids [$HNO_3(aq)$ and $HClO_4(aq)$].

Because a principal aim of the present work was to obtain heat capacities and volumes for selected aqueous species, two kinds of complications were addressed. Chemical considerations required that since many of the solutions investigated contained more than one electrolyte, appropriate versions of Young's rule or Pitzer's theory were used to extract desired single electrolyte properties from measured properties for these mixed electrolyte solutions. It was also necessary to analyze the measured (total) heat capacities in terms of appropriate sums of the heat capacities of the solute species plus contributions due to "chemical relaxation". Relaxation contributions from partially dissociated solutes in the presence of inert electrolytes in one case, and in the presence of electrolytes actively participating in the dissociation reaction in the other, are presented.

The standard state heat capacities of many ions have been used in rigorous calculations of the thermodynamic properties of these ions over the temperature range of the present measurements. These same data were used along with existing semi-theoretical equations of state to derive extrapolated thermodynamic properties (Gibbs free energies, equilibrium constants, and an important standard electrode potential) to much higher temperatures. These calculations have led to a generalized

method for estimating some thermodynamic properties of hydrolyzed species of 3+ aqueous metal ions.

The standard state heat capacities reported here have made a substantial contribution to a critical review of previously published heat capacities. These critically reviewed heat capacities have been used to develop a new model and correlative scheme for estimating heat capacities of unknown aqueous species.

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Chapter 1

Introduction

This thesis is comprised of 20 chapters, 18 of which deal in various ways with thermodynamic studies, both experimental and theoretical, of aqueous electrolyte solutions. Several different experimental and theoretical techniques have been used to provide thermodynamic data that are of fundamental importance for a description of the physical processes associated with many thermodynamic properties and also for the calculation of many other classical thermodynamic properties.

A large fraction of the thesis describes the use of flow microcalorimetric and densimetric equipment for the determination of such fundamental thermodynamic properties as partial molar volumes and heat capacities of aqueous solutions.

All of these measurements have led to various classical thermodynamic calculations involving various integral properties of partial molar volumes and heat capacities (namely predicting the temperature and pressure dependence of equilibrium constants or free energies, and also the temperature dependence of enthalpies and entropies). The results have also been used in testing various existing theories and correlations for the thermodynamic properties of aqueous electrolyte solutions as well as novel semi-theoretical calculations. These calculations involve models for the solvation of gaseous ions, models for the prediction of the thermodynamic properties of metal hydrolyzed species, and extensions of the applicability of chemical relaxation calculations to solutions containing mixed electrolytes and systems comprised of two or more coupled equilibria.

The final portion of the thesis is devoted to reviews of two main areas of data for aqueous electrolytic species. The first involves a critical survey of thermodynamic properties for complexation of aqueous metal cationic species by EDTA, and the second a critical compilation of most modern heat capacity data for aqueous electrolytes.

where V is the volume associated with the system and dp is the corresponding change in pressure associated with a change in the Gibbs free energy of dG. The presence of a term including volume in this equation immediately displays the importance of this quantity in calculations involving chemical equilibria.

The following equation is easily derived from eq. 2.2

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{2.3}$$

where the pressure dependence of the Gibbs free energy for a system is equal to the volume of that system. Since the classical definition of the heat capacity (at constant pressure) is

$$C_p = \frac{q_p}{\Delta T} \tag{2.4}$$

valid only for small values of ΔT because of the temperature dependence of the heat capacity, combination of eq. 2.4 with the first and second laws leads to

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \tag{2.5}$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \tag{2.6}$$

These expressions clearly show the importance of the heat capacity function in determining the temperature dependence of the entropy and enthalpy that in turn may be used to determine the temperature dependence of the Gibbs free energy. These equations show one application of the knowledge of volumes and heat capacities of systems that can lead to calculations of other important properties including the Gibbs free energies over ranges of temperature and pressure.

2.2 Experimental Equipment

2.2.1 Picker flow microcalorimeter

There are several different experimental techniques that have been used to obtain the specific heat or heat capacity of aqueous solutions containing dissolved electrolytes. Historically, these measurements have been made with batch calorimeters that accurately measure known amounts of energy input and the corresponding temperature change that permits calculation of the heat capacity by use of eq. 2.4.

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These calorimeters were (and are) quite accurate for concentrated solutions but become much less accurate for solutions of low concentrations of solute (where the measurements are most important). The principal importance of the Picker flow microcalorimeter (PICKER *et al.*, 1971) lies in its use for the measurement of heat capacities of dilute solutions.

The Picker calorimeter is shown schematically in Figure 2.1. It consists of two symmetrical cells that consist of hollow tubes to which are connected heaters (Zener diodes) and sensitive temperature sensors (thermistors). The heat capacity of a solution can be determined by the following equation:

$$\sigma = \frac{W}{\dot{f}\Delta T} \tag{2.7}$$

Here σ is the volumetric specific heat capacity, W is the electric power input to the heater, $\dot{f}$ is the volumetric flow rate of the liquid through the cell, and ΔT is the temperature rise produced by the combination of flow rate and electric power. This equation could be used to determine the volumetric heat capacity of a liquid but this would be inferior to using a batch calorimeter because of problems associated with maintaining and measuring constant flow rates. The symmetrical nature of this instrument (twin cells), however, makes it particularly suited for the measurement of ratios in heat capacities of two liquids as opposed to the absolute measurement described above. The relative measurement is performed by passing the unknown liquid through one of the cells and a liquid of known heat capacity through the other. The cells of the calorimeter are connected in series, thus insuring identical flow rates for the liquids flowing through both cells as depicted in Figure 2.1. Different liquids are introduced into the calorimeter by the use of liquid chromatography valves that allow neat switching of flow. The presence of a delay line (situated between the two cells) ensures that for some time interval one liquid is one cell while the other liquid is in the other. A more detailed account of the operation of this calorimeter follows.

The instrument is tuned by measuring the power inputs required to produce an identical temperature rise in each of the cells (normally a rise of 2°C) when water is made to flow (at the same rate) through the cells. The electronically operated thermal feedback and control unit then maintains the exact temperature rise in both cells by matching differences in thermistor output resistances from both of the

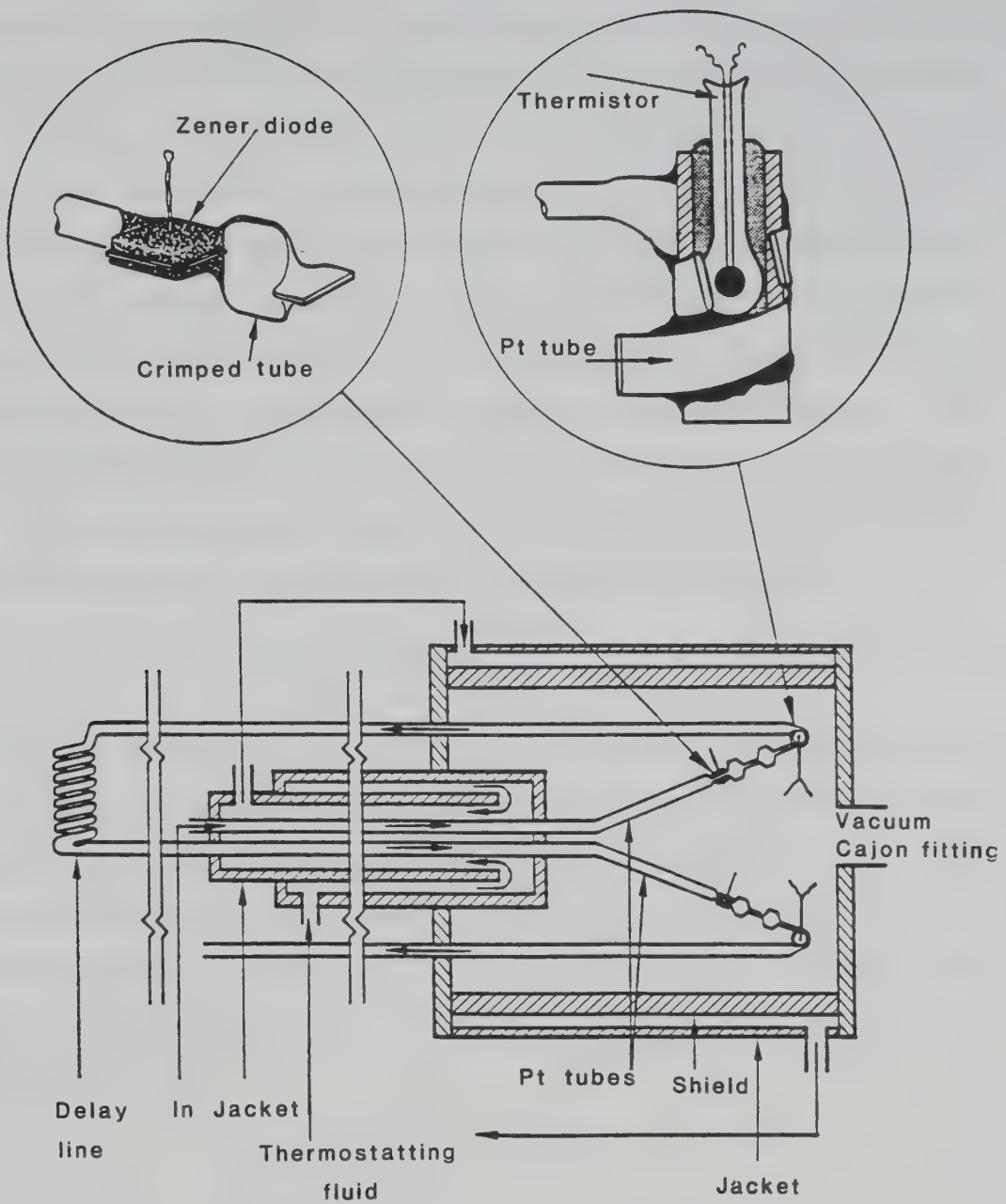

Figure 2.1: Schematic diagram of the Picker flow microcalorimeter, modified from PICKER *et al.* (1971).

cells. An experiment is performed by first balancing and tuning the calorimeter using water to normalize the amount of power required by the measurement cell to produce the same temperature rise as that exhibited in the reference cell. The actual run begins by flowing water for a long enough period to produce a baseline signal (zero difference between reference and measurement cell) and then switching to a sample of solution (same flow rate obtained by gravity feed or by constant flow pumps) into the calorimeter as can be visualized in Figures 2.1 and 2.2. The thermal feedback circuit adjusts the power supplied to the heater associated with the measurement cell thus achieving a temperature rise in this cell exactly equal to that in the reference cell. This difference in power (output as a difference in voltage because of constant current) is monitored by a chart recorder or computer. This signal is directly proportional to the difference between the volumetric heat capacity of the solution in the measurement cell and the water in the reference cell. The ratio of volumetric heat capacities of the two solutions can be calculated from

$$\frac{\sigma_{samp} - \sigma_{ref}}{\sigma_{ref}} = \frac{\Delta W_1}{W_\circ} \tag{2.8}$$

where σ_{samp} and σ_{ref} are the heat capacities per unit volume of the liquids flowing through the measurement cell (solution) and reference cell (water), ΔW_1 is the difference in power between measurement and reference cells required to maintain the same temperature rise in both cells, and $W_\circ$ is the average power applied to both heaters. Since the present interest is in heat capacities per mole of substance, these volumetric heat capacities must be converted into specific heat capacities using the densities of the two solutions:

$$\frac{c_{p,samp}}{c_{p,ref}} = \frac{d_{ref}}{d_{samp}}\left(1 + \frac{\Delta W_1}{W_\circ}\right) \tag{2.9}$$

Here $c_{p,samp}$ and $c_{p,ref}$ are the specific heat capacities of solution and water and d_{samp} and d_{ref} are the corresponding densities.

Eventually there will be enough of the solution flowing through the calorimeter that it will completely fill the delay line and will start to flow through both cells simultaneously. The output signal should then return to the initial position generated from the water/water baseline. At this point, the same amount of power should be required to raise the temperature of the solution by the preset amount in each of

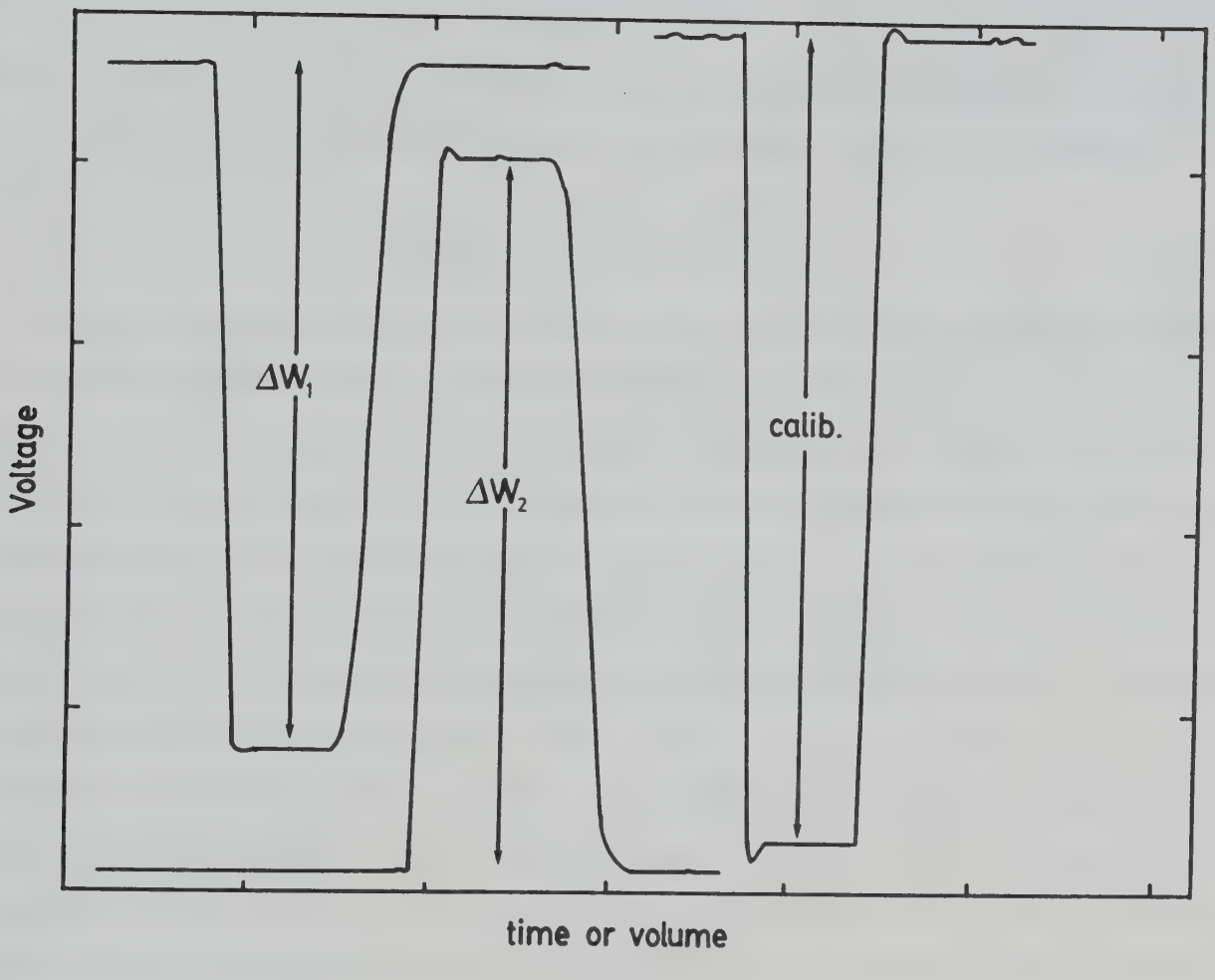

Figure 2.2: Typical plot of the output voltage of the thermal detection unit as a function of time for a complete experimental run with the Picker flow microcalorimeter.

the cells. The experiment is completed by switching the flow of liquid back to water, which creates a difference in the applied power to the two cells because of the adjustment of power output to the measurement cell that maintains a temperature rise in this cell equal to that in the reference cell. This deflection is in the opposite direction to that produced in the first portion of the experiment. The magnitude of this signal is related to the volumetric heat capacities by

$$\frac{\sigma_{ref} - \sigma_{samp}}{\sigma_{samp}} = \frac{\Delta W_2}{W_o} \tag{2.10}$$

This can be rearranged with consideration of the densities of solutions to yield the ratio of the specific heat capacity of the reference fluid to that of the sample:

$$\frac{c_{p,ref}}{c_{p,samp}} = \frac{d_{samp}}{d_{ref}} \left(1 + \frac{\Delta W_2}{W_o}\right) \tag{2.11}$$

Figure 2.2 shows the complete plot of a typical experimental run with the Picker flow microcalorimeter. There are two peaks (ΔW_1 and ΔW_2) that permit calculation of the ratio of specific heats of solution to water. Immediately following (normally) or preceding the experimental run, the differential ouput of the calorimeter is calibrated by the application of a known amount of power to the heater in the reference cell (see Figure 2.2). The deflections produced by the variation of the power to the measurement cell during the course of the experimental run are easily referenced to this known amount of electrical power, which then can be used in eqs. 2.9 and 2.11 for the calculation of the specific heat capacities. The absolute precision of the differential signal output of the Picker calorimeter is of the order of the precision and accuracy of batch calorimeters (0.1 to 0.3 %). However, the signal from the Picker flow calorimeter represents directly the difference (or ratio) of the heat capacity of the solution and reference. So long as the heat capacity of the reference liquid is known accurately (true for water), the determined heat capacity of the unknown liquid should also be accurate (the Picker flow calorimeter generally produces heat capacities of aqueous solutions referenced to water with a precision of one part in 10^4). Since only the difference in specific heat for a solution and water (as discussed later) is required, this calorimeter gives us a direct and accurate measurement. There have been no calorimeters developed that yield more accurate heat capacities of dilute aqueous solutions to date.

It was noted (DESNOYERS *et al.*, 1976; WHITE and WOOD, 1982) that the Picker flow calorimeter suffers from very small heat losses due to slight assymmetries in the two cells. This heat leak is normally assessed by the measurement of the specific heat of a relatively concentrated aqueous solution of NaCl. The heat leak correction factor f is defined in terms of eq. 2.7 by

$$f = \frac{W}{\dot{f}\Delta T\sigma} \tag{2.12}$$

where all symbols were defined previously. The heat leak correction factor f is always greater than unity denoting a smaller ΔT than expected (in measurements on a calibration substance such as a solution of NaCl in water or on a solution of unknown heat capacity).

All of the heat capacity experiments were performed using a Picker flow microcalorimeter (Sodev model CP-C) specially fitted with platinum cells for the study of severely corrosive solutions. The calorimeter was connected to a Sodev thermal detection (balance) unit (model DT-C) that was used for tuning and calibrating the calorimeter and for output of the differential calorimetric signal, and to a Sodev high flow, high stability circulating fluid pump, and a precise temperature control unit (models PC-B and CT-L). The differential output voltage of the thermal detection unit was recorded on a large size Hewlett-Packard X-Y recorder (model HP 7045B) capable of plotting deflections greater than 34 cm in height. Calibration voltages and currents were acquired using a Hewlett-Packard digital multimeter (HP 3465A). Temperature was monitored by a thermistor (Omega type 44107) calibrated against a Hewlett-Packard quartz crystal thermometer (HP 2804A), which itself was calibrated at the ice point of water. Thermistor resistances were measured with a Hewlett-Packard HP 3456A digital voltmeter. It was found that heat losses were greatly reduced by the construction of a moderately high vacuum system to evacuate the region between the two calorimetric cells. This vacuum line was constructed out of 1 inch copper tubing and 1/2 inch flexible tubing equipped with a Cajon O-ring fitting for connection to the calorimeter. A vacuum of less than 10^{-4} mbar was maintained with a Sargeant Welch belt type roughing pump (model 1400) and CVC products diffusion pump (model VMF-10). The pressure was monitored by both an Edwards Penning (type 8) and Edwards Pirani (type 11) gauges. The appropriate

data resulting from the calorimeter were stored in a Hewlett-Packard computer (HP 86B) for further analysis using BASIC programs written specifically for each type of system under study. Copies of these programs are available from the author.

2.2.2 Vibrating tube densimeter

As mentioned in the previous section, densities of solutions are required to convert volumetric heat capacities obtained using the Picker flow microcalorimeter into specific heat capacities that are required in various thermodynamic calculations. Densities of solutions are also useful as they can be used to calculate the volumes of substances or in this case the volumes of aqueous solutions. There are many accurate methods for the measurement of the densities of aqueous solutions. One of the best methods in terms of a balance of speed, accuracy, and convenience is the vibrating tube densimeter.

The densities of all solutions were obtained by the use of a Picker type vibrating tube flow densimeter (PICKER *et al.*, 1974). Vibrating tube densimeters are based on the principle that the natural oscillation frequency of a tube is dependent on the total mass of the tube. Thus the natural oscillation frequency can be used to determine the density of a liquid flowing through that tube since the amount of fluid that is contained in the tube depends on the fluid's density. The natural vibration period (1/frequency) of a tube is related to the density of a fluid flowing through it by (KRATKY *et al.*, 1969)

$$d = c + k\tau^2 \tag{2.12}$$

where c and k are constants unique to the mechanical characteristics of the vibrating tube assembly. Figure 2.3 shows a schematic diagram of a Picker type vibrating tube flow densimeter.

The constants defined by eq. 2.12 can be obtained by the measurement of the time periods of two substances of known density. The calibration constant k of the densimeter can be calculated from

$$k = \frac{d_2 - d_1}{\tau_2^2 - \tau_1^2} \tag{2.13}$$

where d_1 and d_2 are the known densities of the two substances and τ_1 and τ_2 are the corresponding time periods for these two substances. The substances tradition-

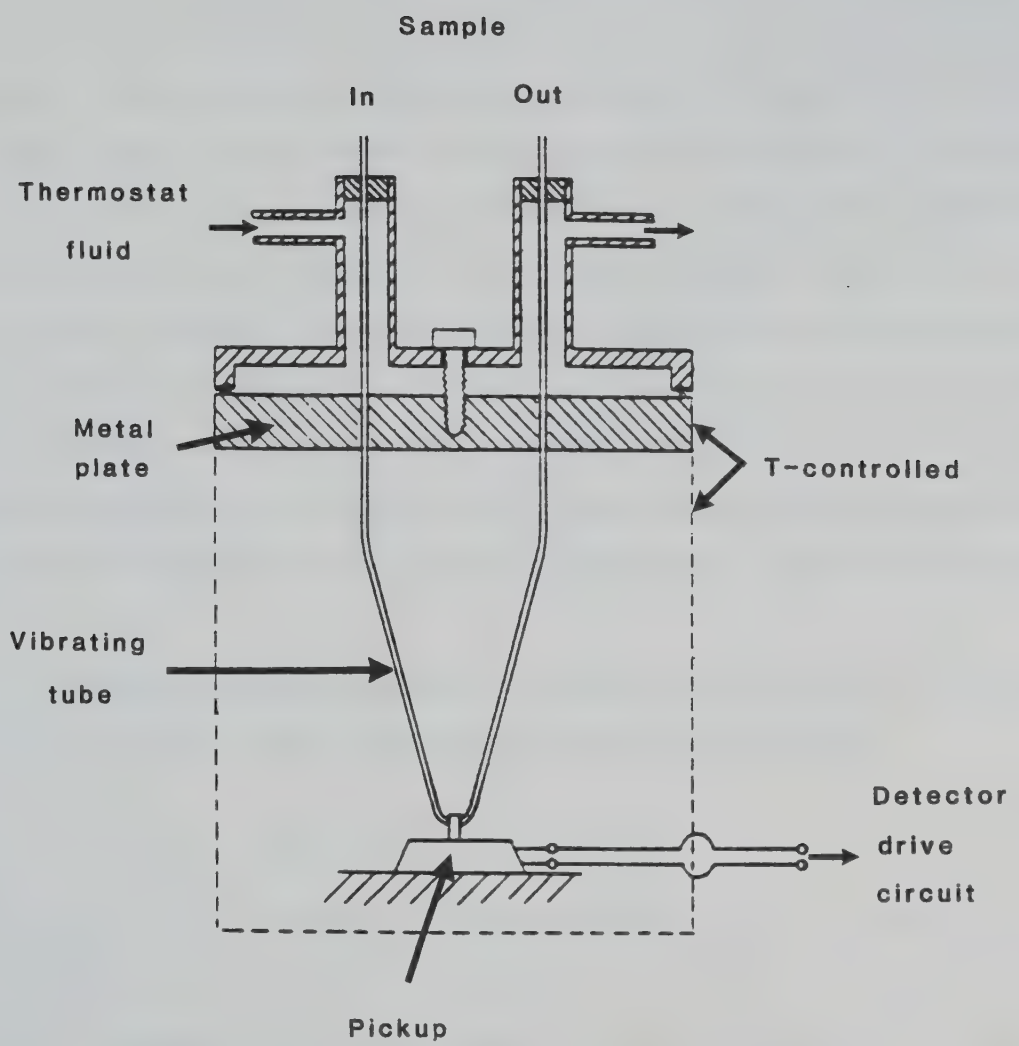

Figure 2.3: Schematic diagram of the Picker type vibrating tube flow densimeter modified after PICKER *et al.* (1974).

ally used for this purpose were water [d = 0.997047 g cm^{-3} (KELL, 1967))] and pure nitrogen gas [$d = 11.455 \times 10^{-4}$ g cm^{-3} (NBS circular 564)]. The vibrating tube densimeter used in these studies was equipped with a platinum vibrating tube, whereas most other instruments are equipped with stainless steel tubes. The mechanical characteristics of a platinum tube (deformability etc.) made the calibration procedure using nitrogen and water unsatisfactory. The results obtained with this densimeter for various aqueous solutions containing NaCl resulted in calculated densities outside of the normal limits of uncertainty for these types of densimeters. It was found that calibration of the instrument with a 1 molal NaCl solution and water resulted in calculated densities to well within expected uncertainties. The calibration constant k defined through eq. 2.13 for densimeters with platinum tubes is not constant through the range 1.455×10^{-4} to approximately 1.2 g cm^{-3} in density. All measurements were thus made by calibrating the instrument with a fluid of known density somewhere in the range of the experimental measurements (always using concentrated NaCl solutions) where the calibration constant should remain constant.

Once the densimeter has been calibrated (k calculated), the density of an aqueous solution can be calculated when referenced to water by the equation

$$d_{sol} = d_{H_2O} + k(\tau_{sol}^2 - \tau_{H_2O}^2) \tag{2.14}$$

where d_{H_2O} and d_{sol} are the densities of water and solution and τ_{H_2O} and τ_{sol} are the corresponding time periods. An experimental run is illustrated in Figure 2.4. There are three distinct regions to the plot. Regions 1 and 3 are traces of the observed time period of the tube when pure water is flowing through the cell. Region 2 is the observed trace when solution is introduced into the densimeter. The absolute values of the average time periods for each of these regions permits calculation of the densitites by way of eq. 2.14.

All densities were obtained using a Picker type flow densimeter (Sodev model 03-D) connected to a high speed, high stability circulating pump and a temperature control unit (Sodev models PC-B and CT-L). Temperature was monitored by a thermistor placed in the circulating fluid lines. This thermistor was calibrated by the same procedure as that for the calorimeter. Thermistor resistances were measured

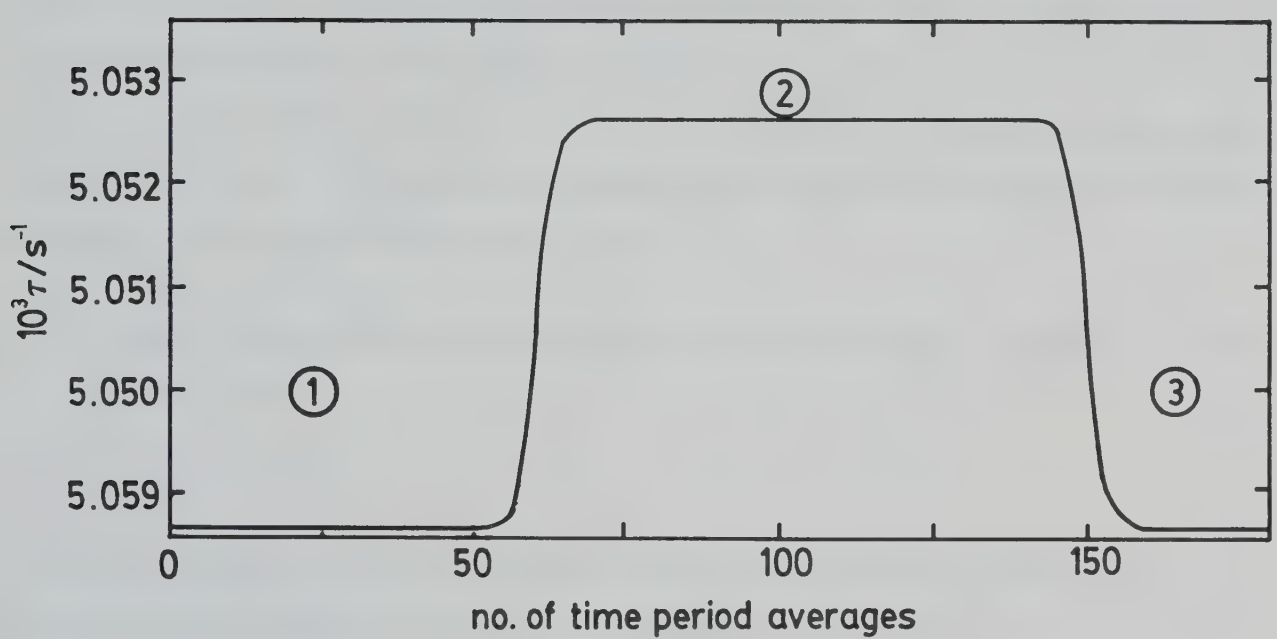

Figure 2.4: Typical time period output during a normal determination of the density of an aqueous solution with a Picker type flow densimeter.

with a Hewlett-Packard digital voltmeter (HP 3456A). Time periods were determined using a Hewlett-Packard universal counter (HP 5316A) by averaging the counts acquired for 30 seconds (the internal clock speed of the counter is 10 MHz). The universal counter was interfaced to a Hewlett-Packard HP 86B computer through a Hewlett-Packard HP-IB interface. Normally 160 of these 30 second average time periods generated by the universal counter were collected by the computer for each experimental run. These recorded time periods were averaged over specified intervals (baseline, peak etc.) by computer. These averages normally were made on no less than 40 of the recorded average time periods. Each time period measurement thus employed approximately 1.2×10^8 counts from the universal counter. The maximum resolution of this counting procedure was determined to be much higher than the normal observed standard deviation for each portion of the experiment most likely due to very slight local inhomogeneity of the aqueous solutions and slight perturbations in flow rate. The average precision of the absolute time periods (30 second averages) was normally better than 1 ppm.

2.3 Heat Capacities and Volumes for Simple Aqueous Electrolytes

2.3.1 Introduction

As discussed earlier, heat capacities and volumes of substances are useful for classical thermodynamic calculations and for testing models that describe the thermodynamic properties of ions in water (and other solvents). Heat capacities and volumes are related to equilibrium constants[4] by the following equations

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \tag{2.15}$$

$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_p = \Delta C_p^\circ \tag{2.16}$$

[4]Equilibrium constants are related to the change in the standard state free energy by $\Delta G^o = -RT\ln K$ where ΔG^o is the standard state change in free energy and K is the equilibrium constant. ΔG^o is the change in free energy when all elements or species are in their designated standard states. For elements this standard state is usually the most stable (or common) phase of the species at 298.15 K. Standard states for aqueous solutions will be discussed later. The standard state change in free energy can be most easily related to the equilibrium constant in terms of the chemical potential as discussed later in section 2.3.3

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta V^\circ}{RT} \tag{2.17}$$

where superscript ○ denotes thermodynamic properties in their standard states (PITZER and BREWER, 1961). Standard state heat capacities and volumes can thus be used to calculate the temperature dependence of equilibrium constants (if the enthalpy is known), the pressure dependence of equilibrium constants, and the temperature dependence of the standard state enthalpy.

Models for predicting many thermodynamic properties for aqueous ions must satisfy both the equilibrium properties (Gibbs free energies) as well as derivative properties (enthalpy, entropy, volume, etc.). It is these derivative properties that often show whether or not a particular model is valid. The present volumes and heat capacities of aqueous solutions provide severe tests of such models and further data that can be used to develop new (improved) models.

Heat capacity and volume data for many aqueous electrolytes have been obtained previously and are discussed at length in Chapter 18. However, many aqueous species that are of interest are normally complicated by experimental problems such as solubility limitations or the presence of undesirable side reactions in solutions containing these species, thus limiting the quantity of data available. The bulk of the measurements described in the following chapters are connected with this latter group of aqueous electrolytes. The treatment that has been applied to experimental results for the simplest of the systems that we have investigated is presented here.

Calorimetric and densimetric measurements on aqueous solutions containing $HClO_4$, HNO_3, $(CH_3)_4NOH$, and K_2SO_4 at 298.15 K have been made. These electrolytes are free of the complications cited above but their properties are useful in their own right and are needed here in connection with analyzing results for aqueous species complicated by competing side reactions and the presence of additional electrolytes as discussed later in this thesis. For this purpose, our requirements were for data at higher concentrations than previously obtained, and for new data for one of the electrolytes [$(CH_3)_4NOH$]. These results permit evaluation of standard state (infinite dilution) partial molar properties from which improved values for the corresponding properties of some of the constituent ions of these electrolytes have been determined.

2.3.2 Experimental

Water to be used for all experiments was passed through an activated charcoal filter and then through a Milli-RO4/Milli-Q reagent grade mixed bed ion exchange column and activated carbon system to yield purified water with a resistivity of 18 MΩ cm or greater. Concentrated perchloric and nitric acids were obtained from Fisher (certified, ACS) and were used without further purification. A 25% aqueous solution of tetramethylammonium hydroxide was obtained from Alfa (certified, ACS) and was used without further purification. Certified crystals of potassium sulphate were obtained from Fisher. Stock solutions of $HClO_4$, HNO_3, and $(CH_3)_4NOH$ were prepared from the concentrated aqueous solutions by dilution with water. The acids were standardized by titration against tris(hydroxymethyl)-aminomethane (THAM) using bromocresol green as indicator. The stock solution of $(CH_3)_4NOH$ was standardized by titration against potassium hydrogen phthalate (KHP) using phenolphthalein as indicator. Four replicates of all titrations were done with resulting overall deviations of less than 0.1 % . The stock solution of K_2SO_4 was prepared by mass after drying the salt at 110°C for several hours.

Densities and heat capacities of all solutions were measured with a Sodev model 03D Picker flow densimeter (PICKER *et al.*, 1974) and a Sodev model CP-C Picker flow microcalorimeter (PICKER *et al.*, 1971) as described earlier in this chapter. Both the densimeter and calorimeter were controlled to (298.15 ± 0.01) K and held at constant (± 0.001 K) temperature with separate Sodev model CT-L circulating baths. The operating temperatures for both instruments were monitored with thermistors that had been calibrated against a Hewlett-Packard 2804A quartz thermometer and placed in the circulating fluid lines immediately preceding the measurement cells. The densimeter was calibrated with water and concentrated (0.95 to 1.00 molal) solutions of NaCl (PICKER *et al.*, 1974). Measured heat capacities were corrected for small heat leaks as suggested by DESNOYERS *et al.* (1976) ; the correction factor f was evaluated daily and was found to be 1.006 ± 0.002.

2.3.3 Partial molar properties

Partial molar properties are most conveniently described in terms of consideration of the total differential of the Gibbs free energy. For a substance of constant composition, the Gibbs free energy is a function of temperature and pressure only

$$G = G(T, p) \tag{2.18}$$

The total differential of the Gibbs free energy can be written as

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp \tag{2.19}$$

For systems of variable composition, however, there can be changes in the Gibbs free energy due only to changes in the number of moles of each species present in the system. Hence for systems containing variable amounts of several species, the Gibbs free energy is a function of T, p, and the amount of substance (moles) present,

$$G = G(T, p, n_1, n_2, ..., n_i, ...) \tag{2.20}$$

where n_i represents the number of moles of species i. The total differential for the Gibbs free energy for these types of systems is

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \sum \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j \neq n_i} dn_i \tag{2.21}$$

The third term is simplified by introducing the definition of the chemical potential for species i, μ_i (PITZER and BREWER, 1961).

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j \neq n_i} \tag{2.22}$$

Partial molar properties are defined generally by

$$\bar{Y} = \left(\frac{\partial Y}{\partial n_i}\right)_{T,p,n_j \neq n_i} \tag{2.23}$$

It is now apparent that the chemical potential μ_i is equal to the partial molar Gibbs free energy $\bar{G}_i$.[5]

[5]The chemical potential was originally defined by G.N. Lewis. He described the chemical potential as a measure of the *escaping tendancy* of that substance. For example, in the case of a solute distributed between two immiscible liquid phases at constant temperature and pressure, the phase in which the species has the higher chemical potential will be depleted of the solute until the chemical potential of the solute in both phases becomes equal. This clearly shows that the difference in chemical potential for these two species at equilibrium is zero.

All of the thermodynamic equations that describe the relationship between the Gibbs free energy and derivatives of the Gibbs free energy with respect to temperature and pressure are valid for the corresponding relations with partial molar properties. For example, the following equations show these relationships for partial molar volumes:

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad \rightarrow \left(\frac{\partial \bar{G}_i}{\partial p}\right)_T = \left(\frac{\partial \mu_i}{\partial p}\right)_T = \bar{V}_i \tag{2.24}$$

2.3.4 Results and Calculations

Results of measurements with the Picker flow calorimeter are volumetric heat capacities (J $K^{-1}cm^{-3}$). Combination of these with the densities that have also been measured permits calculation of specific heat capacities (J $K^{-1}g^{-1}$) and thence the desired apparent molar heat capacities (${}^{\phi}C_p$) of the solutes. Similarly, densities of the solutions lead to apparent molar volumes (${}^{\phi}V$) of the solutes. These apparent molar heat capacities and volumes are defined by equations of the type

$${}^{\phi}Y_2 = \frac{Y_{sol} - n_1 Y_1^{\circ}}{n_2} \tag{2.25}$$

in which Y_{sol} is the extensive property (heat capacity or volume) of a specified quantity of solution, n_1 is the amount (moles) of solvent in this specified quantity of solution, Y_1° is the molar property (heat capacity or volume) of pure solvent (water), and n_2 is the amount (moles) of solute in the specified quantity of solution.

The experimetal quantities that come directly from measurements with the Picker flow calorimeter and densimeter are $[(c_p d/c_{p,1}^{\circ} d_1^{\circ}) - 1]$ (see eq. 2.9) and $(d - d_1^{\circ})$. Directly useful equations for calculations of apparent molar heat capacities and volumes, which also permit recovery of our experimental specific heat capacities and densities, are the following:

$${}^{\phi}V_2 = \frac{\frac{1 + mM_2}{d} - \frac{1}{d_1^{\circ}}}{m} \tag{2.26}$$

$${}^{\phi}C_{p,2} = \frac{c_p(1 + mM_2) - c_{p,1}^{\circ}}{m} \tag{2.27}$$

In these equations m is the molality of the solution, M_2 is the molar mass of the

solute, d and d_1° are the densities of solution and of pure water, and c_p and $c_{p,1}^\circ$ are the specific heat capacities of solution and of pure water. The values $c_{p,1}^\circ = 4.1793$ J $K^{-1}g^{-1}$ and $d_1^\circ = 0.997047$ g cm^{-3} from KELL (1967, 1972) have been used in these calculations. Since the Picker calorimeter results in determination of the heat capacity ratio for solution and solvent (water), this ratio is first used to calculate c_p for the solution and also for calculations defined by eq. 2.27. Results of all of our measurements on the electrolytes under present consideration are summarized in Table 2.1.

The apparent molar function was suggested by G.N. Lewis as a method of determining partial molar quantites. An apparent molar property for a solute in water can be thought of as the "apparent" volume that n_2 moles of the solute contributes to a volume of solution containing n_1 moles of solvent. For example, eq. 2.25 can be rearranged into the form

$$Y_{sol} = n_1 Y_1^\circ + n_2 {}^\phi Y_2 \tag{2.28}$$

where all symbols were defined previously. If 1 mole of NaCl is added to 1000 g of water, the change in volume of the solution represents the apparent molar volume of the solute. By considering the definition of partial molar properties (eq. 2.23) eq. 2.28 can be differentiated with respect to n_2 (holding n_1 constant) to obtain

$$\bar{Y}_2 = {}^\phi Y_2 + n_2 \left(\frac{\partial {}^\phi Y_2}{\partial n_2} \right)_{T,p,n_1} \tag{2.29}$$

Equation 2.29 can be used along with ${}^\phi Y_2$ values obtained over a range of concentrations to calculate the corresponding partial molar properties.

At infinite dilution, $n_2 = 0$ and the important relationship $\bar{Y}_2^\circ = {}^\phi Y_2^\circ$ holds. Here the superscript $\circ$ indicates the thermodynamic standard state.

Apparent molar properties of aqueous electrolytes are represented satisfactorily to moderate ionic strengths by Debye-Hückel equations of the form:

$${}^\phi Y_2 = \bar{Y}_2^\circ + A_Y \omega I^{1/2} + B_Y I + C_Y I^{3/2} \tag{2.30}$$

in which ${}^\phi Y_2^\circ$ is the desired standard state (infinite dilution) partial molar property, A_Y is the Debye-Hückel limiting slope, ω is the "valence factor", I is the ionic strength, and B_Y are C_Y are adjustable parameters. The ionic strength, valence

Table 2.1: Compositions of solutions, densities, heat capacities, and apparent molar volumes and heat capacities for aqueous HNO_3, $HClO_4$, K_2SO_4, and $(CH_3)_4NOH$ at 25°C.

m (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	${}^\phi V_2$ (cm^3 mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	${}^\phi C_{p,2}$ (J K^{-1}mol^{-1})
		$HClO_4$		
1.0588	5.6403	44.65	−4.271	8.79
0.87073	4.6703	44.71	−3.617	5.22
0.71850	3.8791	44.71	−3.064	1.63
0.61269	3.3221	44.72	−2.646	0.21
0.51356	2.7970	44.72	−2.254	−2.08
0.41412	2.2656	44.71	−1.848	−4.44
0.28819	1.5852	44.72	−1.315	−7.56
0.19110	1.0589	44.54	−0.888	−11.01
0.09494	0.5292	44.45	−0.452	−15.39
		HNO_3		
1.1115	3.5247	30.23		
1.1115	3.5219	30.26	−4.042	−31.84
0.85809	2.7420	30.22	−3.245	−37.07
0.81123	2.5963	30.22	−3.101	−38.62
0.61416	1.9797	30.18	−2.423	−43.11
0.47135	1.5271	30.15	−1.907	−46.75
0.34271	1.1170	30.08	−1.423	−50.90
0.22793	0.7466	30.02	−0.967	−54.43
0.11160	0.3681	29.91*	−0.484	−58.32*
		$(CH_3)_4NOH$		
0.88135	0.4472	85.93	−4.585	122.7
0.88135	0.4553	85.84		
0.68384	0.3500	85.97	−3.691	117.9
0.60701	0.3088	86.04	−3.321	116.4
0.49297	0.2530	86.04	−2.734	115.3
0.35938	0.1855	86.07	−2.053	110.9
0.29242	0.1517	86.07	−1.693	108.9
0.20339	0.1062	86.08	−1.196	106.9
0.10948	0.0571	86.12*	−0.658	103.4

Table 2.1 (continued)

m (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	${}^\phi V_2$ (cm^3 mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	${}^\phi C_{p,2}$ (J K^{-1}mol^{-1})
		K_2SO_4		
0.49662	6.4949	40.58	−3.371	−121.8
0.40229	5.3132	39.80	−2.852	−136.7
0.32377	4.3146	39.04	−2.369	−148.7
0.32377	4.3148	39.04		
0.25841	3.4731	38.25	−1.954	−161.4
0.17242	2.3441	37.15	−1.362	−179.3
0.11097	1.5229	36.18	−0.912	−195.8
0.07858	1.0850	35.50	−0.660	−205.8
0.03623	0.5057	34.20*	−0.316	−223.7*

* These values were not used in the least squares analyses, but are shown in the Figures.

factor, and molality are related by

$$I = \omega m = \frac{1}{2}\sum m_i z_i^2 \tag{2.31}$$

Values used for the Debye-Hückel slopes were $A_C = 32.783$ J $K^{-1}kg^{1/2}mol^{-3/2}$ and $A_V = 1.8743$ $cm^3kg^{1/2}mol^{-3/2}$ (BRADLEY and PITZER, 1979; ANANTHASWAMY and ATKINSON, 1984).

Equations of type 2.30 are derived from the non-extended Debye-Hückel theory (DEBYE and HÜCKEL, 1923) for ionic solutes in water. The direct result of Debye-Hückel theory relates the activity coefficient of a solution to properties of the pure solvent, and the concentration of the solute:

$$\ln\gamma_{\pm} = -A_\gamma \mid z_+ z_- \mid I^{1/2} \tag{2.32}$$

Here $\gamma_{\pm}$ is the mean ionic activity coefficient, z_+ and z_- are the charges of two ions making up the solute and the constant A_γ is defined by (PITZER, 1979)

$$A_\gamma = \left(\frac{2\pi N_\circ d_w}{1000}\right)^{1/2}\left(\frac{e^2}{DkT}\right)^{3/2} \tag{2.33}$$

where $N_\circ$ is Avagadro's number, d_w is the density of solvent (water), e is the charge of an electron, D is the dielectric constant of the solvent (water), k is Boltzman's constant, and T is the temperature. Values of the A parameters for partial molar volumes (A_V) and heat capacities (A_C) can be derived by using standard thermodynamic relations between the natural logarithm of the activity coefficient and these properties. The activity coefficient was defined by G.N. Lewis (PITZER and BREWER, 1961) as

$$\mu_i - \mu_i^\circ = RT\ln a_i \tag{2.34}$$

where $\mu_i - \mu_i^\circ$ represents the difference in the chemical potential between some state of given activity (a) and some standard state where the activity ($a_\circ$) is defined equal to 1 for species (solute) i. The derivatives of the chemical potential are related to derivatives of activity and to derivatives of the activity coefficient as shown following.

The activity coefficient (molality composition scale) of a solute is defined in terms of the activity by

$$\gamma_2 = \frac{a_2}{m_2} \tag{2.35}$$

where m_2 is the molality of a solution containing the solute designated as component 2. In the limit of the infinitely dilute solution, the familiar result of activity being equal to molality (activity coefficient of 1) results (HARNED and OWEN, 1958). The activity of a completely dissociated solute (designated by a_2) in water is related to the thermodynamically defined mean ionic activity (PITZER and BREWER, 1961) by

$$a_2 = a_+^{\nu_+} a_-^{\nu_-} = a_\pm^{\nu} \tag{2.36}$$

where a_+ and a_- are the activities of positive and negative ions, ν_+ and ν_- are the numbers of positive and negative ions making up the solute, ν is the total numbers of constituent ions in the solute ($\nu = \nu_+ + \nu_-$), and $a_\pm$ is the mean ionic activity of the solute.

Expressions that relate the A_Y parameters (from Debye-Hückel theory) to experimental determinations of apparent molar volumes and heat capacities can now be derived. The derivative of the chemical potential with respect to pressure can be defined as

$$\left[\frac{\partial(\mu - \mu_\circ)}{\partial p}\right]_T = \bar{V} - \bar{V}^\circ \tag{2.37}$$

since $\mu_i - \mu_i^\circ = RT\ln a_i$ and the mean ionic activity coefficient $a_\pm$ is related to the activity coefficient of the solute a_i by $a_\pm = a_i^{\frac{1}{\nu}}$. Thus the following expression is obtained

$$\left(\frac{\partial \ln \gamma_\pm}{\partial p}\right)_T = \frac{\bar{V} - \bar{V}^\circ}{\nu RT} \tag{2.38}$$

Combining eqs. 2.32 and 2.38 leads to

$$\bar{V}_2 = \bar{V}_2^\circ + \frac{\nu}{2} \mid z_+ z_- \mid I^{1/2} \left[2RT\left(\frac{\partial A_\gamma}{\partial p}\right)_T\right] \tag{2.39}$$

All Debye-Hückel slopes for the higher derivative partial molar properties are defined by the quantities located in the square brackets (PITZER and BREWER, 1961) with appropriate substitution of the other partial derivatives of A_γ, depending on the partial molar property. Therefore for partial molar volumes the slope is defined by

$$\bar{A}_V = 2RT\left(\frac{\partial A_\gamma}{\partial p}\right)_T \tag{2.40}$$

Similarly for heat capacities the expression for $\bar{A}_C$ is given by

$$\bar{A}_C = -2RT^2\left(\frac{\partial^2 A_\gamma}{\partial T^2}\right)_p \tag{2.41}$$

These equations for $\bar{A}_C$ and $\bar{A}_V$ are for partial molar properties (consistent within the derivation using the partial molar Gibbs free energies). The general equation that is predicted from Debye-Hückel theory for the concentration dependence of partial molar properties (as in eq. 2.39) is

$$\bar{Y} = \bar{Y}^\circ + \frac{\nu}{2}\bar{A}_Y \mid z_+ z_- \mid I^{1/2} \tag{2.42}$$

which is normally applicable only in the very dilute region. The quantities $\frac{\nu}{2} \mid z_+ z_- \mid$ may be collected together and recast in terms of the definition of the valence factor ω (eq. 2.31) to obtain the expression

$$\bar{Y} = \bar{Y}^\circ + \bar{A}_Y \omega I^{1/2} \tag{2.43}$$

Debye-Hückel slopes for partial molar properties are related to those for apparent molar properties as are the corresponding partial and apparent molar quantities by eq. 2.29. The ionic strength dependence of apparent molar properties can be expressed by

$$^\phi Y = \bar{Y}^\circ + A_Y \omega I^{1/2} \tag{2.44}$$

where A_Y is related to $\bar{A}_Y$ (using eq. 2.29) by $A_Y = \frac{2}{3}\bar{A}_Y$. Equation 2.44 is the limiting law form of eq. 2.30 presented earlier. The apparent molar volumes and heat capacities obtained at finite ionic strengths can now be fit with expressions of the type given by eq. 2.30.

Least squares fits of equations of type 2.30 to the results listed in Table 2.1 have led to the values of $^\phi C_p^\circ$, B_C, C_C, $^\phi V^\circ$, B_V, and C_V that are listed in Table 2.2. To illustrate the quality of these fits, graphs of $^\phi Y$ - $A_Y \omega I^{1/2}$ against I are shown in Figs. 2.5 and 2.6.

Estimates of uncertainties in the present $^\phi C_p^\circ$ and $^\phi V^\circ$ values for $(CH_3)_4NOH$ are $\pm$ 4 J $K^{-1}mol^{-1}$ and $\pm$ 0.4 cm^3mol^{-1}. Estimated uncertainties for aqueous $HClO_4$ and HNO_3 are $\pm$ 2 J $K^{-1}mol^{-1}$ and $\pm$ 0.2 cm^3mol^{-1}, with estimated uncertainties for aqueous K_2SO_4 intermediate between the values listed here for other electrolytes.

2.3.5 Discussion

Both direct and indirect comparisons can be made of the results with results from earlier investigators, as follows.

Table 2.2: Standard state (infinite dilution) partial molar heat capacities, volumes, B_Y, and C_Y parameters at 298.15 K.*

Solute	${}^{\phi}V_2^{\circ}$ ($cm^3 mol^{-1}$)	B_V ($cm^3 kg\ mol^{-2}$)	C_V ($cm^3 kg^{3/2} mol^{-5/2}$)
$HClO_4$	43.99 ± 0.02	-1.201 ± 0.032	
HNO_3	29.32 ± 0.02	-0.955 ± 0.023	
$(CH_3)_4NOH$	85.54 ± 0.03	-1.609 ± 0.048	
K_2SO_4	32.41 ± 0.05	2.033 ± 0.21	-0.9415 ± 0.16

Solute	${}^{\phi}C_{p,2}^{\circ}$ ($JK^{-1} mol^{-1}$)	B_C ($J\ kg\ K^{-1} mol^{-2}$)	C_C ($J\ kg^{3/2} K^{-1} mol^{-5/2}$)
$HClO_4$	-25.5 ± 0.2	0.1025 ± 0.39	
HNO_3	-71.6 ± 0.2	4.662 ± 0.32	
$(CH_3)_4NOH$	92.1 ± 0.5	-1.098 ± 1.0	
K_2SO_4	-256.7 ± 0.8	47.43 ± 10.9	-25.67 ± 14

* The $\pm$ values are the statistical uncertainties (standard deviations) associated with the fit of eq. 2.30 to our experimental results. Total uncertainties are larger than these $\pm$ values, as discussed in the text.

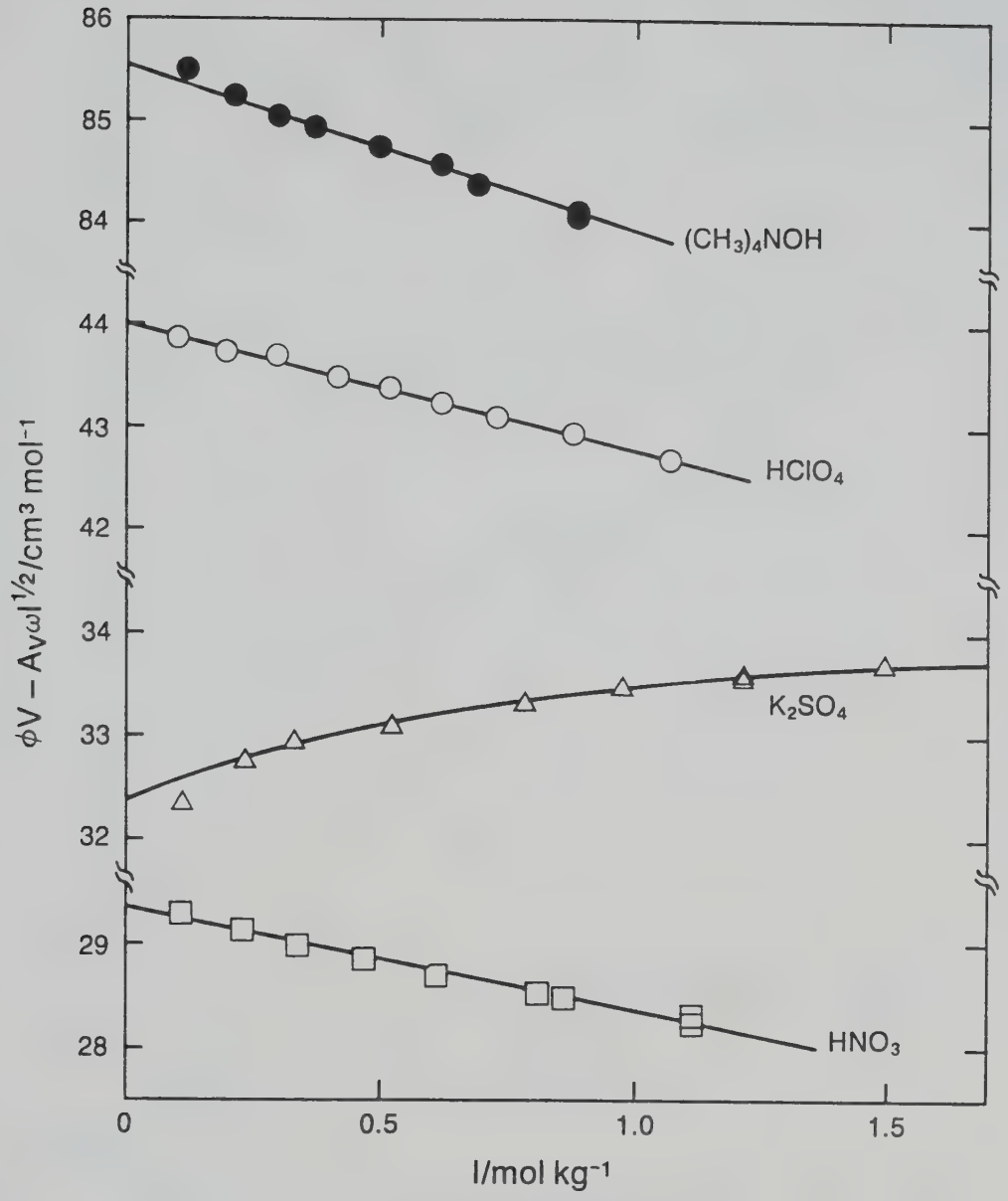

Figure 2.5: ${}^{\phi}V$ minus the Debye-Hückel limiting slope ($A_V \omega I^{1/2}$) for aqueous $HClO_4$, HNO_3, $(CH_3)_4NOH$, and K_2SO_4 against I. Lines are least squares fits of eq. 2.30

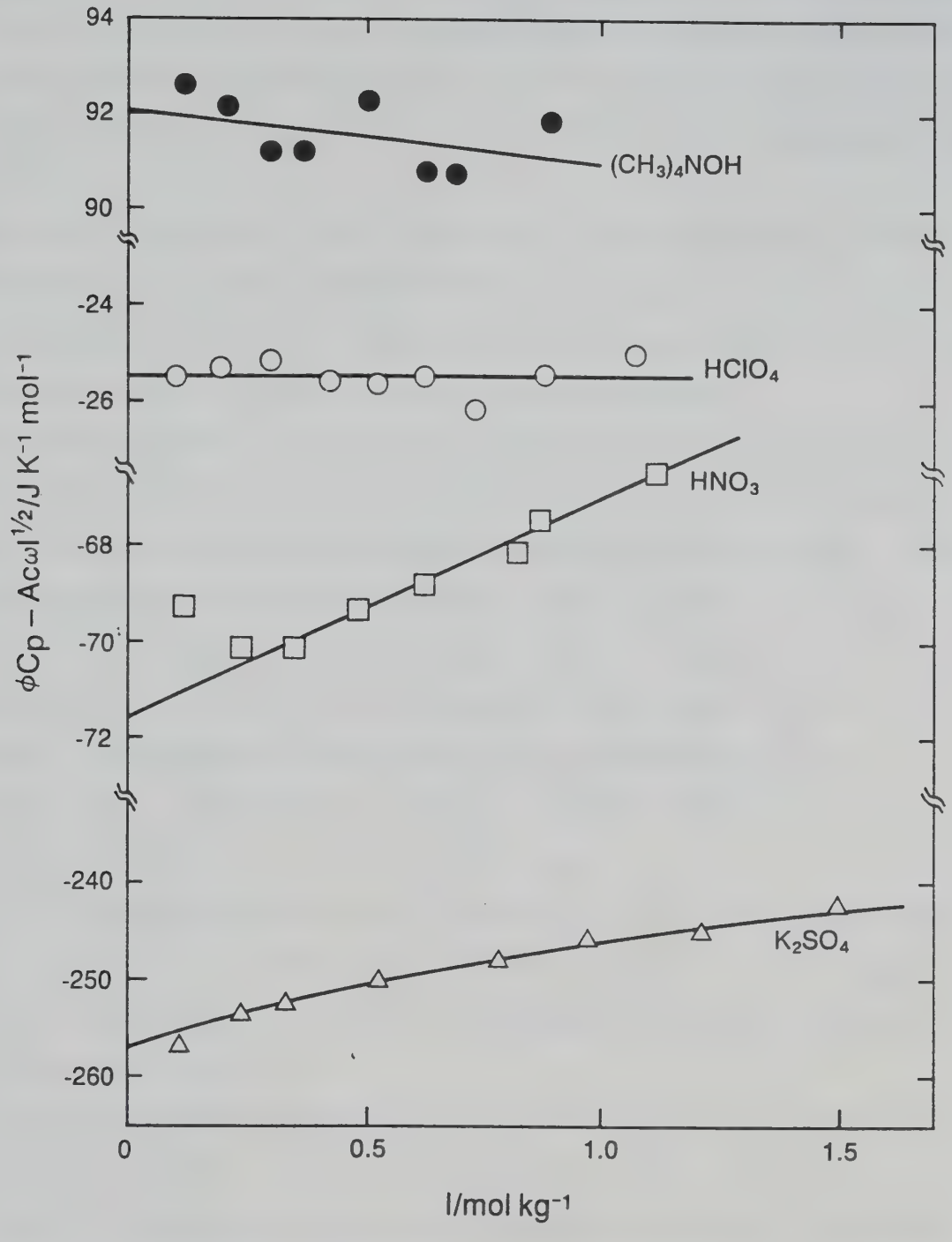

Figure 2.6: ${}^{\phi}C_p$ minus the Debye-Hückel limiting slope ($A_C\omega I^{1/2}$) for aqueous $HClO_4$, HNO_3, $(CH_3)_4NOH$, and K_2SO_4 against I. Lines are least squares fits of eq. 2.30

The present ${}^{\phi}V^{\circ}(HClO_4) = 43.99$ cm^3mol^{-1} is in excellent agreement with 44.04 cm^3mol^{-1} listed by MILLERO (1972) and 44.097 cm^3mol^{-1} reported by HERRINGTON *et al.* (1985) on the basis of their recent direct measurements. The average of these three values is ${}^{\phi}V^{\circ}(HClO_4) = 44.04$ cm^3mol^{-1}, which is adopted as the best available value. The consistency of ${}^{\phi}V^{\circ}$ values for several electrolytes is demonstrated by the reasonable agreement of this direct value with 44.2 cm^3mol^{-1} calculated indirectly by ROUX *et al.* (1978).

The value ${}^{\phi}C_p^{\circ}(HClO_4) =$ -27.1 J $K^{-1}mol^{-1}$ from SINGH *et al.* (1977) is in fair agreement with the present -25.5 J $K^{-1}mol^{-1}$. Combination of ${}^{\phi}C_p^{\circ}$ values for several electrolytes has led ROUX *et al.* (1978) to a corresponding -25 J $K^{-1}mol^{-1}$. We select ${}^{\phi}C_p^{\circ}(HClO_4) =$ -25.5 J $K^{-1}mol^{-1}$ as the best available value.

Values of ${}^{\phi}V^{\circ}(HNO_3) = 29.3$ cm^3mol^{-1} from direct measurements by ENEA *et al.* (1977) and 29.5 cm^3mol^{-1} calculated by ROUX *et al.* (1978) from ${}^{\phi}V^{\circ}$ values for several electrolytes, along with 29.0 cm^3mol^{-1} listed in Millero's tabulation (MILLERO, 1972) are available. The present ${}^{\phi}V^{\circ}(HNO_3) = 29.32$ cm^3mol^{-1} is in good agreement with all of these values. The selected "best" value is ${}^{\phi}V^{\circ}(HNO_3) = 29.3$ cm^3mol^{-1}.

The present ${}^{\phi}C_p^{\circ}(HNO_3) =$ -71.6 is in excellent agreement with -72.1 J $K^{-1}mol^{-1}$ from direct measurements by ENEA *et al.* (1977) and with -72 J $K^{-1}mol^{-1}$ calculated by ROUX *et al.* (1978) from ${}^{\phi}C_p^{\circ}$ values for several electrolytes. The value -72 J $K^{-1}mol^{-1}$ is selected as the best available value.

For ${}^{\phi}V^{\circ}(K_2SO_4)$ values from the literature (MILLERO, 1972 ; OLOFSSON *et al.*, 1978 ; PERRON *et al.*, 1975) range from 30.1 to 32.8 cm^3mol^{-1} compared with the present value (32.41 cm^3mol^{-1}). Our weighted average of all these results is ${}^{\phi}V^{\circ}(K_2SO_4) = 32.2$ cm^3mol^{-1}.

Previous investigators (DESNOYERS *et al.*, 1976 and PERRON *et al.*, 1975; OLOFSSON *et al.*, 1978) have reported ${}^{\phi}C_p^{\circ}(K_2SO_4) =$ -251.0 J $K^{-1}mol^{-1}$ and -254.5 J $K^{-1}mol^{-1}$. Recalculations using their experimental results in combination with the revised (BRADLEY and PITZER, 1979; ANANTHASWAMY and ATKINSON, 1984) value of A_C and the present results leads to a selected ${}^{\phi}C_p^{\circ}(K_2SO_4) =$ -256 J $K^{-1}mol^{-1}$.

There have been no previous calorimetric or densimetric measurements on aqueous $(CH_3)_4NOH$, but measurements on solutions of tetramethylammonium halides have led to results that can be used for indirect comparisons. Volumetric data from

PERRON and DESNOYERS (1972) and from HEPLER *et al.* (1965) for tetramethylammonium halides in combination with data for sodium halides and sodium hydroxide (DESNOYERS *et al.*, 1976 ; ROUX *et al.*, 1978 ; FORTIER *et al.*, 1974 ; DESNOYERS *et al.*, 1969 ; ROUX *et al.*, 1984 ; ALLRED and WOOLLEY, 1981) lead to calculated values of ${}^{\phi}V^{\circ}[(CH_3)_4NOH]$ from 85.3 to 85.6 cm^3mol^{-1}. On the basis of these values and the present result, the selected value is ${}^{\phi}V^{\circ}[(CH_3)_4NOH] = 85.5$ cm^3mol^{-1}.

Heat capacities of solutions of the tetramethylammonium halides from DESNOYERS *et al.* (1976 ; PHILIP *et al.*, 1972 ; PERRON *et al.*, 1976) in combination with heat capacities of solutions of sodium halides and sodium hydroxide (DESNOYERS *et al.*, 1976 ; ROUX *et al.*, 1978 ; FORTIER *et al.*, 1974 ; DESNOYERS *et al.*, 1969 ; ROUX *et al.*, 1984 ; ALLRED and WOOLLEY, 1981) lead to values of ${}^{\phi}C_p^{\circ}[(CH_3)_4NOH]$ from 94 to 98 J $K^{-1}mol^{-1}$. Considerations of chemical problems suggests that the lowest of these values is probably the best. On this basis and in consideration of the present value (92.1 J $K^{-1}mol^{-1}$), the selected value is ${}^{\phi}C_p^{\circ}[(CH_3)_4NOH] = 94$ J $K^{-1}mol^{-1}$.

The selected values of ${}^{\phi}C_p^{\circ}$ and ${}^{\phi}V^{\circ}$ can now be used for calculation of the useful partial molar properties (standard state, infinite dilution) of ions based on the conventions that ${}^{\phi}C_p^{\circ}(H^+,aq) \equiv 0$ and ${}^{\phi}V^{\circ}(H^+,aq) \equiv 0$. The selected values for the standard state partial molar properties of $HClO_4(aq)$ and $HNO_3(aq)$ lead directly to the desired conventional ${}^{\phi}C_p^{\circ}$ and ${}^{\phi}V^{\circ}$ for $ClO_4^-(aq)$ and $NO_3^-(aq)$, as listed in Table 2.3. Combination of ${}^{\phi}V^{\circ}(K^+) = 9.02$ cm^3mol^{-1} from MILLERO (1972) with the ${}^{\phi}V^{\circ}$ for aqueous K_2SO_4 leads to ${}^{\phi}V^{\circ}(SO_4^{2-}) = 14.2$ cm^3mol^{-1}. Similarly, ${}^{\phi}C_p^{\circ}(K^+) = 13$ J $K^{-1}mol^{-1}$ from ROUX *et al.* (1978) leads to ${}^{\phi}C_p^{\circ}(SO_4^{2-}) = -282$ J $K^{-1}mol^{-1}$. The standard state partial molar properties of both $(CH_3)_4N^+(aq)$ and $OH^-(aq)$ are defined more accurately by way of properties of electrolytes other than the $(CH_3)_4NOH(aq)$ that we have investigated.

The standard state (infinite dilution) properties of aqueous electrolytes are additive, as illustrated by the calculations described in the preceding paragraph and also earlier in this paper. In contrast to this additivity, the parameters such as B_Y, that are used in the Debye-Hückel equation (2.30) to represent the properties of solutions at moderate ionic strengths, are not additive. The values of these parameters for $(CH_3)_4NOH(aq)$ can be calculated (by assuming additivity) from data for aqueous tetramethylammonium halides in combination with data for sodium halides and

Table 2.3: Conventional [$^{\phi}Y^{\circ}(H^+, aq) \equiv 0$] standard state partial molar volumes and heat capacities for aqueous ions at 298.15 K.

Ion	$\bar{V}^{\circ}$ (cm^3mol^{-1})	$\bar{C}_p^{\circ}$ ($JK^{-1}mol^{-1}$)
ClO_4^-	44.04	−25.5
NO_3^-	29.3	−72
SO_4^{2-}	14.2	−282

sodium hydroxide are not the same as the values obtained from our results and listed here in Table 2.2. Calculations of this type provide a range of B_Y values (depending on the halide chosen) that are far outside our estimated uncertainties of these values. The direct B_Y values listed in Table 2.2, are the preferred values, and are useful in ways that were mentioned previously.

2.4 References

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Chapter 3

Heat capacities and volumes of aqueous mixed electrolyte systems: Mercury(II) and lead(II) perchlorates at 298.15 K[1]

3.1 Introduction

Thermodynamic properties of the aqueous ions of mercury and lead are important for a variety of applications to geochemical, industrial, environmental, and health-related problems. We already have reliable values for the Gibbs free energy, enthalpy, and entropy at 298.15 K for both $Hg^{2+}(aq)$ and $Pb^{2+}(aq)$, cited in the compilation by WAGMAN *et al.* (1982). There are, however, no published values for standard state partial molar heat capacities of either of these aqueous ions. MILLERO (1972) has cited earlier investigations leading to standard state partial molar volumes of aqueous solutions of some salts of both $Hg^{2+}(aq)$ and $Pb^{2+}(aq)$, but there are problems with these results that require further examination. As a result of these considerations, measurements of the heat capacities and densities of aqueous solutions containing $Hg(ClO_4)_2$ and $Pb(ClO_4)_2$ in dilute perchloric acid were undertaken at 298.15 K. The presence of this additional acid introduces minor complications in the data treatment that will be discussed later.

One purpose of this work has been to provide reliable heat capacity and volume values for use in various classical thermodynamic calculations, such as those involving the temperature and pressure dependence of Gibbs energies and related equilibrium properties. Another purpose has been to extend the base of thermodynamic property values that can be used in testing and possibly improving various empirical or theoretical correlations of the properties of aqueous ions.

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3.2 Experimental

All of these heat capacity measurements have been made with a Picker flow calorimeter (PICKER *et al.*, 1971) (Sodev model CP-C) as described in Chapter 2. Operation of this calorimeter has been checked as previously recommended (DESNOYERS *et al.*, 1976), leading to correction for small heat leaks, with f values near 1.006 as evaluated daily. Densities of solutions have been measured with a Picker flow densimeter (PICKER *et al.*, 1974) (Sodev model 03D), which was calibrated with pure water and with sodium chloride solutions of known (PICKER *et al.*, 1974) densities. The calorimeter was controlled to a mean temperature of (298.15±0.02) K and the densimeter was controlled to (298.15±0.01) K with separate circulating baths (Sodev model CT-L) that were held constant to ± 0.001 K. Temperatures were monitored with thermistors that had been calibrated against a Hewlett-Packard quartz thermometer and placed in the circulating fluid immediately in front of each of the calorimeter and densimeter cells.

Water to be used in all solutions was passed through an activated charcoal filter and then through a Milli-RO4/Milli-Q reagent grade mixed-bed ion exchange column and activated carbon system to yield purified water with resistivity greater than 18 MΩ cm. Concentrated perchloric acid from Fisher (certified, ACS) was used without further purification. Crystalline hydrates of $Hg(ClO_4)_2$ and $Pb(ClO_4)_2$ obtained from Alfa (certified as > 99 mass per cent) and from G. Frederick Smith (certified as > 99.9 mass per cent), respectively, were recrystallized from dilute aqueous $HClO_4$. Stock solutions were then prepared by dissolving these recrystallized salts (containing some adsorbed or occluded perchloric acid) in dilute aqueous perchloric acid.

The lead perchlorate stock solution was analyzed for total lead by a direct ammoniacal EDTA titration with sodium-potassium tartrate and Eriochrome Black T as the indicator, as described by SCHWARZENBACH and FLASCHKA (1969) and FLASCHKA (1964). The molality of perchloric acid in this solution was evaluated from results of careful measurements of pH. Total mercury in the mercuric perchlorate stock solution was determined by titration with a standard potassium thiocyanate solution (FISCHER and PETERS, 1968). The perchloric acid in this solution was determined in two ways. The first involved passing aliquots of stock solution

through a cation exchange resin (Fisher, Rexyn 101H) in the acidic form and then titrating the solution with standardized NaOH solution. The second (probably better) method used direct titration of aliquots of stock solution with standardized NaOH solution. Results from both methods were in good agreement (0.4 per cent) with each other; the slightly higher results obtained from the direct titration measurements were chosen for further calculations. Other solutions were prepared by diluting the stock solutions with dilute, standardized perchloric acid solutions.

3.3 Results and calculations

Results of measurements with the Picker flow calorimeter are volumetric heat capacities relative to the volumetric heat capacity of pure water (PICKER *et al.*, 1971). Combination of these quantities with the densities that have also been measured permits calculation of specific heat capacities of solutions and thence the desired apparent molar heat capacities of the solutions. Similarly, densities of the solutions lead to apparent molar volumes of the solutions. Because the concern here is with mixed electrolyte (metal perchlorate + perchloric acid) solutions, it is convenient and useful to define the "mean" or "experimental" apparent molar properties by

$$^{\phi}Y^{exp} = \frac{Y_{sol} - n_1 Y_1^{\circ}}{n_2 + n_3} \tag{3.1}$$

in which Y_{sol} is the extensive property (heat capacity or volume) of a specified quantity of solution, n_1 is the amount of substance of solvent in this specified quantity of solution, Y_1° is the property (heat capacity or volume) of pure solvent (water), and n_2 and n_3 are the amounts of substance of each of the solutes in the specified quantity of solution.

Equations that permit calculation of the defined "experimental" apparent molar heat capacities and volumes from known molalities and measured specific heats and densities are the following:

$$^{\phi}C_p^{exp} = \frac{c_p(1 + m_2M_2 + m_3M_3) - c_{p,1}^{\circ}}{m_2 + m_3} \tag{3.2}$$

$$^{\phi}V^{exp} = \frac{\frac{1 + m_2M_2 + m_3M_3}{d} - \frac{1}{d_1^{\circ}}}{m_2 + m_3} \tag{3.3}$$

In these equations c_p and $c^\circ_{p,1}$ are the specific heat capacities of the solution and of pure water, and d and d°_1 are the corresponding densities. The molality and molar mass of metal perchlorate are represented by m_2 and M_2; the molality and molar mass of perchloric acid are represented by m_3 and M_3, respectively. Values for the properties of pure water were: $c^\circ_{p,1} = 4.1793$ J $K^{-1}g^{-1}$ and $d^\circ_1 = 0.997047$ g cm^{-3} from KELL (1972,1967).

Results of these calorimetric and densimetric measurements, expressed in terms of molalities and defined (by eq. 3.1) as "experimental" apparent molar heat capacities are given in Table 3.1. The measured specific heats and densities can be recovered from the tabulated quantities and rearranged versions of eqs. 3.2 and 3.3.

Young's rule (YOUNG and SMITH, 1954) was used as the basis for combining apparent molar heat capacities and volumes of aqueous perchloric acid with the "experimental" apparent molar heat capacities and volumes for mixed solutions of (metal perchlorate salt + perchloric acid) to obtain the desired apparent molar properties of $M(ClO_4)_2(aq)$.

Young's rule can be expressed as

$$^\phi Y^{exp} = m_2 \frac{^\phi Y_2}{m_2 + m_3} + m_3 \frac{^\phi Y_3}{m_2 + m_3} + \delta \tag{3.4}$$

In equation 3.4 δ represents

$$\delta = k_{23} \frac{m_2 m_3}{(m_2 + m_3)^2} I \tag{3.5}$$

in which k_{23} is a binary interaction coefficient and I is the molal ionic strength. The apparent molar properties of single electrolytes represented by $^\phi Y_2$ are those for an ionic strength of the single electrolyte equal to the total ionic strength of the mixed electrolyte to which $^\phi Y^{exp}$ refers.

Apparent molar properties of strong electrolytes can be represented by Debye-Hückel equations of the type

$$^\phi Y_2 = \bar{Y}^\circ_2 + A_Y \omega I^{1/2} + B_Y I + C_Y I^{3/2} \tag{3.6}$$

in which $^\phi Y^\circ_2$ is the value of $^\phi Y_2$ at infinite dilution, A_Y is derived from the Debye-Hückel theory, and B_Y and C_Y are adjustable parameters. The ionic strength I and

Table 3.1: Results of calorimetric and densimetric measurements at 298.15 K for solutions of $Hg(ClO_4)_2$, and $Pb(ClO_4)_2$ in $HClO_4$.

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d-d_1^\circ)$ (g cm^{-3})	ϕV^{exp} (cm^3 mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ}-1\right)$	ϕC_p^{exp} (J K^{-1}mol^{-1})
			$Hg(ClO_4)_2$		
0.3148	0.0968	10.3705	69.43	−2.588	17.0
0.2049	0.1353	7.1948	64.06	−2.060	6.14
0.2049	0.1353	7.1970	63.99		
0.1778	0.1448	6.4035	62.37	−1.924	3.80
0.1350	0.1598	5.1484	59.32	−1.708	−1.45
0.1350	0.1598	5.1434	59.49		
0.1024	0.1712	4.1886	56.64	−1.532	−3.45
0.08383	0.1777	3.6402	54.87	−1.434	−5.49
0.07011	0.1825	3.2320	53.55	−1.358	−6.26
0.02781	0.1973	1.9759	48.55	−1.118	−9.38
			$Pb(ClO_4)_2$		
0.2827	0.00219	9.2120	72.98	−2.218	−30.5
0.2057	0.00192	6.7443	72.75	−1.673	−41.3
0.1664	0.00178	5.4751	72.57	−1.382	−47.7
0.1233	0.00162	4.0754	72.23	−1.050	−56.0
0.08277	0.00147	2.7477	71.88	−0.7235	−64.2
0.06694	0.00142	2.2267	71.65	−0.5907	−67.0
0.04660	0.00135	1.5551	71.30	−0.4195	−72.6
0.02192	0.00126	0.7386	69.54*	−0.2033	−80.1

* Not included in least squares fits.

the "valence factor" ω are defined and related by

$$I = \omega m = \frac{1}{2}\sum m_i z_i^2 \tag{3.7}$$

Several investigations (YOUNG and SMITH, 1954 ; MILLERO, 1971) have provided evidence that the term represented by δ in equation 3.4 is negligible when $m_2 >> m_3$, as for our measurements on solutions of (lead perchlorate + perchloric acid), or when the total molality $(m_2 + m_3)$ is no more than a few tenths mol kg^{-1}, as is the case for the present solutions. It is therefore expected that $\delta \approx 0$, which was confirmed by least squares fits. The δ term was thus set equal to zero that allows rearrangement of equation (3.4) to obtain

$${}^{\phi}Y_2 = \frac{m_2 + m_3}{m_2}{}^{\phi}Y^{exp} - \frac{m_3}{m_2}{}^{\phi}Y_3 \tag{3.8}$$

The experimental results presented in Table 3.1 were used along with values of ${}^{\phi}C_{p,3}$ for aqueous perchloric acid (Chapter 2) to obtain by way of equation (3.8) the desired values of ${}^{\phi}C_{p,2}$ and ${}^{\phi}V_2$ for $Hg(ClO_4)_2$ and $Pb(ClO_4)_2$ that are listed in Table 3.2.

Least squares fits of equations of types (3.4) to (3.6) to the results in Table 3.2 were done using the values A_C = 32.783 J $kg^{1/2}K^{-1}mol^{-3/2}$ and A_V = 1.8743 $cm^3kg^{1/2}mol^{-3/2}$ from BRADLEY and PITZER (1979) and ANANTHASWAMY and ATKINSON (1984). Values of the parameters obtained from these calculations are listed in Table 3.3 along with associated statistical uncertainties. To illustrate the quality of the fits of equations of type (3.6) to the experimental results, graphs of type $({}^{\phi}Y_2 - A_Y\omega I^{1/2})$ are shown against I in Figure 3.1. *Total* (chemical, calorimetric, etc.) uncertainties in the values of ${}^{\phi}C^{\circ}_{p,2}$ and ${}^{\phi}V^{\circ}_2$ that are of principal interest to us here are about $\pm$ 5 J $K^{-1}mol^{-1}$ and $\pm$ 0.5 cm^3mol^{-1}, respectively.

Although it is both convenient and useful to present the heat capacities and densities of solutions in the form of apparent molar heat capacities and volumes, the corresponding partial molar properties are often more useful for thermodynamic calculations. These partial molar properties $\bar{Y}_2$ of solutes can be calculated from corresponding apparent molar properties by way of

$$\bar{Y}_2 = {}^{\phi}Y_2 + n_2\left(\frac{\partial {}^{\phi}Y}{\partial n_2}\right)_{T,p,n_1} \tag{3.9}$$

which shows that in the limit of infinite dilution, $\bar{Y}^{\circ}_2 = {}^{\phi}Y^{\circ}_2$.

Table 3.2: Calculated values of the hypothetical ${}^{\phi}Y_2$ values for solutions of $Hg(ClO_4)_2$, and $Pb(ClO_4)_2$ in H_2O at 298.15 K.

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	${}^{\phi}V_2$ (cm^{3}mol^{-1})	${}^{\phi}C_{p,2}$ (J K^{-1}mol^{-1})
		$Hg(ClO_4)_2$	
0.3148	0.0968	77.05	19.8
0.2049	0.1353	76.83	8.2
0.2049	0.1353	76.72	
0.1778	0.1448	76.75	5.6
0.1350	0.1598	76.60	−2.2
0.1350	0.1598	76.96	
0.1024	0.1712	76.58	−4.6
0.08383	0.1777	76.42	−8.7
0.07011	0.1825	76.60	−9.7
0.02781	0.1973	76.22	−18.4
		$Pb(ClO_4)_2$	
0.2827	0.00219	73.20	−30.8
0.2057	0.00192	73.01	−41.7
0.1664	0.00178	72.87	−48.2
0.1233	0.00162	72.59	−56.7
0.08277	0.00147	72.37	−65.2
0.06694	0.00142	72.23	−68.2
0.04660	0.00135	72.07	−74.3
0.02192	0.00126	70.99	−83.7

Table 3.3: Standard state (infinite dilution) partial molar heat capacities, volumes, and B_Y and C_Y parameters for aqueous $Hg(ClO_4)_2$ and $Pb(ClO_4)_2$ at 298.15K*.

Solute	${}^{\phi}V_2^{\circ}$ ($cm^3 mol^{-1}$)	B_V ($cm^3 kg\ mol^{-2}$)
$Hg(ClO_4)_2$	73.89 ± 0.15	-2.52 ± 0.20
$Pb(ClO_4)_2$	70.25 ± 0.05	-2.68 ± 0.10

Solute	${}^{\phi}C_{p,2}^{\circ}$ ($JK^{-1}mol^{-1}$)	B_C (J kg $K^{-1}mol^{-2}$)	C_C (J $kg^{3/2}K^{-1}mol^{-5/2}$)
$Hg(ClO_4)_2$	-67.3 ± 1.0	-12.73 ± 1.2	
$Pb(ClO_4)_2$	-107.0 ± 0.5	-40.07 ± 4.5	25.3 ± 4.6

* The $\pm$ values are the statistical uncertainties (standard deviations) associated with the fits of equation (3.6) to our experimental results. Total uncertainties are larger than these $\pm$ values, as discussed in the text.

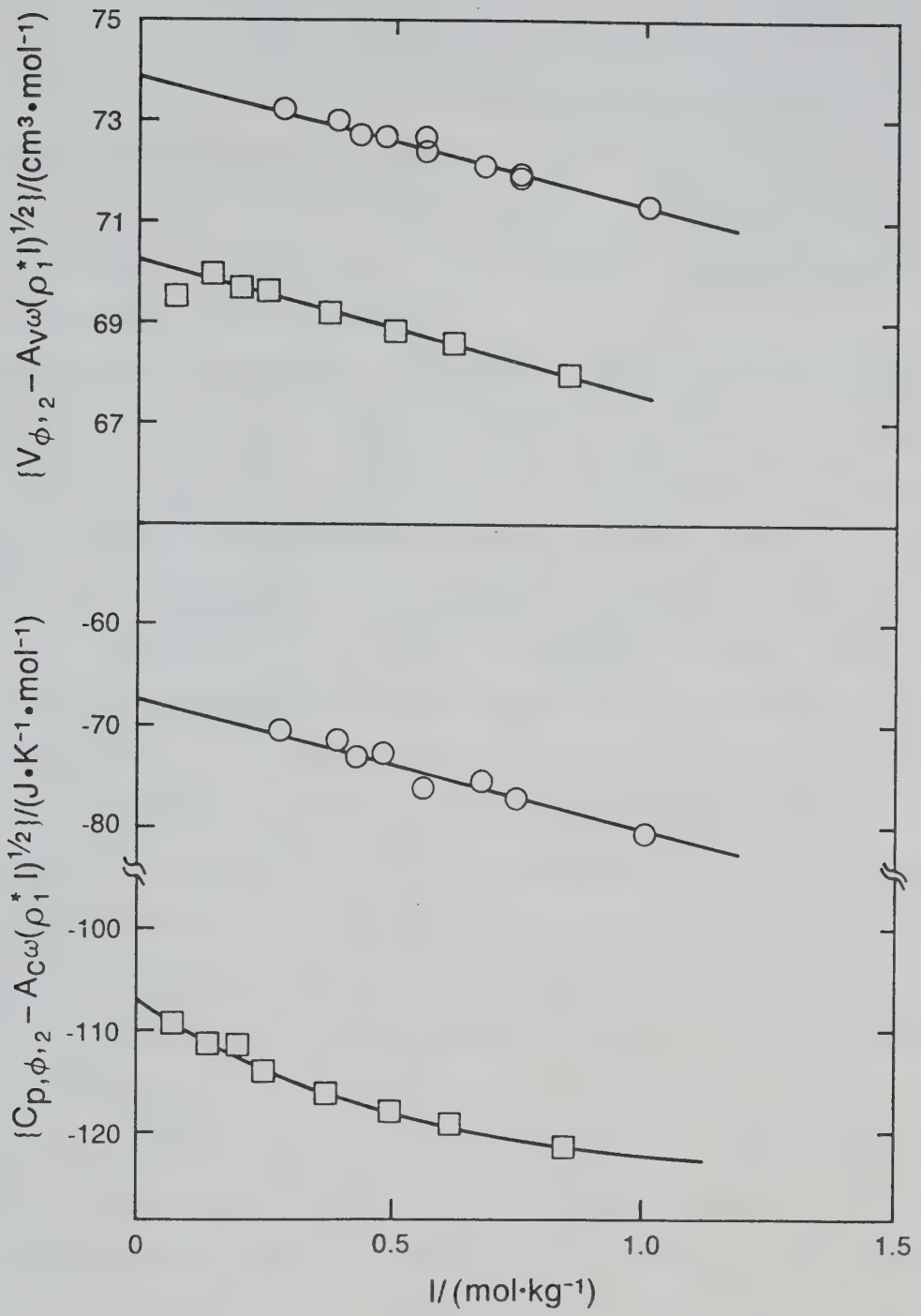

Figure 3.1: ${}^{\phi}Y_2$ minus the Debye-Hückel limiting law term against I. Lines are least squares fits of eq. 3.6.

3.4 Discussion

Consideration of our present results for the standard state partial molar volumes and heat capacities of $Hg(ClO_4)_2$ and $Pb(ClO_4)_2$ listed in Table 3.3, are done most conveniently in terms of "conventional" single ion properties based on $\bar{Y}_2^\circ(H^+) \equiv 0$. The lack of previously previously published accounts of earlier measurements of heat capacities or densities of aqueous solutions containing either $Hg(ClO_4)_2$ or $Pb(ClO_4)_2$ make direct comparisons impossible. Several indirect comparisons of volumes and heat capacities can be made as follows.

MILLERO (1972) has cited $\bar{V}_2^\circ = 16.0$ cm^{3}mol^{-1} for $HgCl_2$(aq) at 298.15 K. Combination of this value with the conventional $\bar{V}_2^\circ(Cl^-) = 17.89$ cm^{3}mol^{-1} from ALLRED and WOOLLEY (1981) leads to $\bar{V}_2^\circ(Hg^{2+}) = -19.8$ cm^{3}mol^{-1}. This cited $\bar{V}_2^\circ$ value for $HgCl_2$(aq) is not quite appropriate for this calculation because of complications due to Hg^{2+} - Cl^- complexes and also hydrolysis of Hg^{2+}(aq) in non-acidic solution (HEPLER and OLOFSSON, 1975 ; BAES and MESMER, 1976). It was to avoid or at least minimize such complications that the present measurements on solutions of mercuric perchlorate in perchloric acid were undertaken. The present $\bar{V}_2^\circ = 73.89$ cm^{3}mol^{-1} for $Hg(ClO_4)_2$(aq) in combination with $\bar{V}_2^\circ(ClO_4^-) = 44.04$ cm^{3}mol^{-1} as listed in Chapter 2, leads to $\bar{V}_2^\circ(Hg^{2+}) = -14.2$ cm^{3}mol^{-1}, which is considered to be the best available standard state partial molar volume for Hg^{2+}(aq).

MILLERO (1972) has listed $\bar{V}_2^\circ = 8.0$ cm^{3}mol^{-1} for $PbCl_2$(aq) and $\bar{V}_2^\circ = 42.5$ cm^{3}mol^{-1} for $Pb(NO_3)_2$(aq). Combination of $\bar{V}_2^\circ(Cl^-) = 17.89$ cm^{3}mol^{-1} from ALLRED and WOOLLEY (1981) and $\bar{V}_2^\circ(NO_3^-) = 29.32$ from Chapter 2 with these volumes leads to $\bar{V}_2^\circ(Pb^{2+}) = -27.8$ and -16.1 cm^{3}mol^{-1}, respectively. In an effort to minimize complications due to Pb^{2+} - Cl^- complex formation and hydrolysis of Pb^{2+}(aq), the present to work was performed with solutions of lead perchlorate in perchloric acid. The present $\bar{V}_2^\circ = 70.25$ cm^{3}mol^{-1} for $Pb(ClO_4)_2$(aq) in combination with the $\bar{V}_2^\circ(ClO_4^-)$ cited above leads to $\bar{V}_2^\circ(Pb^{2+}) = -17.8$ cm^{3}mol^{-1}, which is considered the best available standard state partial molar volume for Pb^{2+}(aq) at 298.15 K.

Values of $\bar{C}_{p,2}^\circ = -67.3$ J K^{-1}mol^{-1} for $Hg(ClO_4)_2$(aq) and $\bar{C}_{p,2}^\circ = -107.0$ J K^{-1}mol^{-1} for $Pb(ClO_4)_2$(aq) have been combined with $\bar{C}_{p,2}^\circ(ClO_4^-) = -25.5$ J K^{-1}mol^{-1} from

Chapter 2 to obtain $\bar{C}^{\circ}_{p,2}(Hg^{2+})$ = -16 J $K^{-1}mol^{-1}$ and $\bar{C}^{\circ}_{p,2}(Pb^{2+})$ = -56 J $K^{-1}mol^{-1}$. No heat capacities for any mercury(II) salts of sufficient precision were found in the literature. Several studies have reported results leading to the heat capacities of solutions containing Pb^{2+}(aq) two of which are worth mention. DRAKIN *et al.* (1967) found for solutions of $Pb(NO_3)_2$ $\bar{C}^{\circ}_{p,2}$ = -226 J $K^{-1}mol^{-1}$ from batch calorimetric results and SERGEEVA *et al.* (1970) found $\bar{C}^{\circ}_{p,2}$ = -190 J $K^{-1}mol^{-1}$ from heats of solution from 18 to 32 °C. These values can be combined with the conventional ionic heat capacity of nitrate ion from Chapter 2 to generate $\bar{C}^{\circ}_{p,2}(Pb^{2+})$ = -82 and -46 J $K^{-1}mol^{-1}$. The former value is in poor agreement with the present result presumably because of hydrolysis and complexation problems at the ionic strengths studied. The latter result is in good agreement with the present value considering that it is based on such a narrow temperature range. It is believed that the present results are the most reliable for $\bar{C}^{\circ}_{p,2}(Pb^{2+})$.

The conventional standard state partial molar heat capacities and volumes for Hg^{2+}(aq) and Pb^{2+}(aq) at 298.15 K that result from this work are listed in Table 3.4 and used as follows.

Several correlations are presently available for the estimation of conventional standard state partial molar volumes and heat capacities for aqueous ions. Most of these schemes are best suited to simple monatomic ions, as is the case here. Conventional standard state partial molar volumes for Hg^{2+}(aq) and Pb^{2+}(aq) have been calculated from the semi-theoretical equations of HEPLER (1957) and SWADDLE and MAK (1983), and the correlations of COUTURE and LAIDLER (1956). Ionic radii as suggested by the authors were used except where no such values were listed. The ionic radius for Hg^{2+}(aq) was not listed by either HEPLER (1957) or COUTURE and LAIDLER (1956). The ionic radius of Hg^{2+}(aq) for both of these correlations, and the ionic radius of Pb^{2+}(aq) for the Hepler correlation were selected from SHANNON (1976). All of these results are summarized in Table 3.4. None of the correlations provides good estimates for the standard state partial molar volumes simultaneously for both species. The equation proposed by HEPLER (1957) shows the best agreement for the prediction of the standard state volume of Hg^{2+}(aq). It is likely due to the difference in the aquated states of both Hg^{2+} and Pb^{2+} to those of most other metal ions that these correlations were based on that make the present predictions

slightly worse than expected.

Values for the heat capacities of these ions have been calculated from the Criss-Cobble entropy correspondence principle CRISS and COBBLE (1964), and the recent correlation of ABRAHAM and MARCUS (1986). The results of these calculations are summarized in Table 3.4. Conventional ionic standard state entropy ($\bar{S}^\circ$) values for Hg^{2+}(aq) and Pb^{2+}(aq) were taken from the listings in the NBS tables (WAGMAN *et al.*, 1981) and ionic radii as described by ABRAHAM and MARCUS (1986). The predictions of both of these models are extremely good. The Criss-Cobble prediction provides excellent estimates of the standard state partial molar heat capacities that differ from the present experimental results by only 6 and 12 J $K^{-1}mol^{-1}$ for Hg^{2+}(aq) and Pb^{2+}(aq), respectively. The predictions of the Abraham and Marcus model are slightly less successful for these two ions than observed for the Criss-Cobble predictions. It is apparent that the Criss-Cobble method is still very useful for the prediction of heat capacities for monatomic mono- or divalent cations, but the principle should be used with care for trivalent cations or complex anions as will be shown in several of the following chapters.

Table 3.4: Conventional $[\bar{Y}_2^\circ(H^+) \equiv 0]$ standard state partial molar volumes and heat capacities for $Hg^{2+}(aq)$ and $Pb^{2+}(aq)$ and comparisons with semi-empirical models at 298.15 K.

	$\bar{V}_2^\circ$ (cm^3mol^{-1})			
Ion	Experiment	HEPLER (1957)	COUTURE and LAIDLER (1956)	SWADDLE and MAK (1983)
Hg^{2+}	−14.2	−12.8	−18.8	−2.7
Pb^{2+}	−17.8	−6.9	−12.7	−12.9

	$\bar{C}_{p,2}^\circ$ ($JK^{-1}mol^{-1}$)		
	Experiment	CRISS and COBBLE (1964)	ABRAHAM and MARCUS (1986)
Hg^{2+}	−16	−22	−69
Pb^{2+}	−56	−44	−80

3.5 References

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Chapter 4

Apparent molar heat capacities and volumes of aqueous $HClO_4$, HNO_3, and H_2SO_4 from 10 to 55 °C: Chemical relaxation in solutions of aqueous sulphuric acid and standard state heat capacities and volumes of ClO_4^-, NO_3^-, and HSO_4^-

4.1 Introduction

Thermodynamic data for aqueous inorganic acids are essential in countless applications where a description of speciation in aqueous environments is required. For example, thermodynamic data are required for nitric and sulphuric acids for calculations involving speciation in many groundwater formations, either naturally occurring or as produced through industrial processes. Aqueous perchloric acid is much less common in natural waters than these other aqueous inorganic salts, yet thermodynamic properties are often required for it as auxiliary data to be used for calculations involving various cationic species. For example, the thermodynamic properties of perchloric acid as a function of temperature are required as auxiliary data for calculations described in Chapters 9 and 13.

The thermodynamic properties of solutions of sulphuric acid, and in particular the bisulphate-sulphate equilibrium, have been studied extensively for over 50 years. A bibliography of most thermodynamic data for the sulphuric acid water system (also the nitric acid and perchloric acid water systems) can be seen in the excellent NBS technical note by SMITH-MAGOWAN and GOLDBERG (1979). There are extensive equilibrium data at room temperature (see for example PITZER *et al.*, 1977), various calorimetric results leading to enthalpies and heat capacities (see for example PITZER, 1937; IZATT *et al.* , 1969; GIAUQUE *et al.*, 1960; KUNZLER and GIAUQUE, 1952; LARSON *et al.*, 1982; RANDALL and TAYLOR, 1941) and also some

volumetric studies that lead to thermodynamic data for aqueous sulphuric acid and the bisulphate-sulphate equilibrium (see for example ROHWER *et al.*, 1975; LARSON *et al.*, 1982). There are also extensive equilibrium studies of reactions involving the bisulphate ion at high temperatures and high pressures (MARSHALL and JONES, 1966; LIETZKE *et al.* 1961; QUIST and MARSHALL, 1966; QUIST *et al.*, 1965; DAWSON *et al.*, 1986), and also some calorimetric results at elevated temperatures (GARDNER *et al.*, 1969; READNOUR and COBBLE, 1969). However, there are only limited data available from modern calorimetric measurements of heat capacities of aqueous solutions and none known at any temperatures other than 25°C.

In this work, the heat capacities and volumes of aqueous solutions containing perchloric, nitric, and sulphuric acids were obtained from 10 to 55°C. No special complications are associated with solutions of perchloric or nitric acid since these solutes appear to be completely dissociated over this temperature range. For solutions containing sulphuric acid, however, the equilibrium involving bisulphate and sulphate ions must be considered when calculating thermodynamic properties of the bisulphate ion since some of this ion is ionized at these temperatures. This ionization reaction introduces complications to both the volumetric and heat capacity results because of speciation, and also further complications to the heat capacity results because of "chemical relaxation" that will be described in detail in a later section of this Chapter.

The calculated volumes and heat capacities of these aqueous species can be used for calculations at elevated temperatures where many of the applications require such data, through the use of simple thermodynamic relationships. The temperature and pressure dependences of the equilibrium constant (or Gibbs free energy) are related to standard state heat capacities and volumes by the expressions :

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \tag{4.1}$$

$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_p = \Delta C_p^\circ \tag{4.2}$$

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = \frac{-\Delta V^\circ}{RT} \tag{4.3}$$

Knowledge of the standard state volume and heat capacity functions thus permit calculation of the equilibrium constants (or Gibbs free energies) as a function of both

temperature and pressure over the experimental temperature range. Combination of these data with semi-theoretical models of ionic hydration permits extrapolation of these data to higher temperatures that are more closely associated with many applications.

4.2 Experimental

Water used for all experiments was first passed through an activated charcoal filter and then through a Milli-RO4/Milli-Q reagent grade mixed bed ion exchange and activated carbon system to yield purified water with a resistivity of 18 MΩ cm or greater. Solutions of NaCl (Fisher certified, ACS) were prepared by mass after drying the salt at 110°C until constant weight.

All stock solutions were prepared from concentrated solutions of the acids. Concentrated (60%) perchloric acid and nitric acid were obtained from Fisher (certified, ACS) and sulphuric acid from Mallinkrodt (SP, ACS). The molality of each stock solution was determined by titration with THAM (perchloric and nitric) and a standard solution of sodium hydroxide (sulphuric). All subsequent solutions were prepared by diluting (by mass) the stock solution with pure water.

The densities of all solutions were measured relative to water at each of the experimental temperatures ± 0.01°C with a Sodev 03D vibrating tube densimeter (PICKER *et al.*, 1974), which was calibrated with pure water and a standard solution of NaCl (results taken from MILLERO, 1970). Heat capacities were measured at the mean reported temperatures ± 0.01°C relative to water with a Sodev CP-C Picker type flow microcalorimeter (PICKER *et al.*, 1971). Temperatures were maintained (constant to ± 0.001°C) in both instruments with separate Sodev CT-L circulating baths and monitored with calibrated thermistors. Daily evaluation of the calorimetric heat loss correction factor (DESNOYERS *et al.*, 1976) by way of measurements on standard solutions of NaCl led to $f = 1.006 \pm 0.002$ at 25°C. This correction factor was assumed to be independent of temperature.

4.3 Results

4.3.1 Apparent molar properties

Table 4.1 lists the experimentally determined relative densities $(d - d_1^\circ)$ and heat capacity ratios $[c_p d/(c_{p,1}^\circ d_1^\circ) - 1]$ for all of the aqueous solutions at each temperature. The apparent molar property ${}^\phi Y$ of a solution is defined generally by

$$ {}^\phi Y_2 = \frac{Y_{soln} - 55.509 Y_1^\circ}{m_2} \tag{4.4} $$

where Y_{soln} is the extensive property (volume or heat capacity) of a solution that contains 1 kg of solvent (water), Y_1° is the molar volume or heat capacity of pure solvent (water), and m_2 is the molality of the solute. Apparent molar volumes and heat capacities were calculated from the results listed in Table 4.1 using the equations:

$$ {}^\phi V_2 = \frac{\frac{1 + m_2 M_2}{d} - \frac{1}{d_1^\circ}}{m_2} \tag{4.5} $$

and

$$ {}^\phi C_{p,2} = \frac{c_p(1 + m_2 M_2) - c_{p,1}^\circ}{m_2} \tag{4.6} $$

where M represents the solute molar mass, c_p and d are the specific heat capacity and density of the solution, and $c_{p,1}^\circ$ and d_1° are the specific heat capacity and density of pure water. Table 4.1 lists values of these apparent molar volumes and heat capacities at temperatures applying to the present measurements.

For solutions of perchloric and nitric acids, these apparent molar properties correspond only to the species present in solution, (ClO_4^-, H^+) and (NO_3^-, H^+), respectively. However, for aqueous solutions containing sulphuric acid, these apparent molar properties contain contributions from all of the species present at equilibrium: (HSO_4^-, H^+) and (SO_4^{2-}, $2H^+$). Apparent molar properties that pertain to a single electrolyte in solution (such as those for nitric and perchloric acids) will be distinguished from those pertaining to more than one electrolytic species (sulphuric acid) by labeling these latter properties "experimental" apparent molar properties. These experimental apparent molar properties must undergo further analysis to permit evaluation of the properties for the species HSO_4^-(aq) that is of particular interest.

Table 4.1: Compositions of solutions, densities, heat capacity ratios, and apparent molar volumes and heat capacities for HNO_3, $HClO_4$, and H_2SO_4 at 10, 25, 40, and 55°C.

m_2 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	${}^\phi V_2$ (cm^3 mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	${}^\phi C_{p,2}$ (J K^{-1}mol^{-1})
		$HClO_4$		
		10°C		
1.0829	5.9961	42.53	−4.717	−14.17
0.8954	4.9956	42.54	−4.031	−19.08
0.7302	4.1049	42.49	−3.384	−23.67
0.6205	3.5059	42.47	−2.935	−26.99
0.5247	2.9827	42.35	−2.532	−30.23
0.4091	2.3349	42.39	−2.023	−34.69
0.2668	1.5381	42.15	−1.365	−41.74
0.1841	1.0647	42.17	−0.960	−45.12
		25°C		
1.0588	5.6403	44.65	−4.271	8.79
0.87073	4.6703	44.71	−3.617	5.22
0.71850	3.8791	44.71	−3.064	1.63
0.61269	3.3221	44.72	−2.646	0.21
0.51356	2.7970	44.72	−2.254	−2.08
0.41412	2.2656	44.71	−1.848	−4.44
0.28819	1.5852	44.72	−1.315	−7.56
0.19110	1.0589	44.54	−0.888	−11.01
0.09494	0.5292	44.45	−0.452	−15.39
		40°C		
1.0829	5.5268	46.80		
1.0829	5.5217	46.85	−4.276	19.59
0.8954	4.6003	46.89	−3.623	16.93
0.7302	3.7780	46.91	−3.017	14.57
0.6205	3.2231	46.96	−2.592	13.74
0.5247	2.7406	46.90	−2.235	10.75
0.4091	2.1492	46.87	−1.772	8.52
0.2668	1.4117	46.83	−1.182	5.34
0.1841	0.9751	46.98	−0.829	3.65

Table 4.1 (continued)

m_2 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	${}^\phi V_2$ (cm^3 mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	${}^\phi C_{p,2}$ (J K^{-1}mol^{-1})
		55°C		
1.0829	5.3949	48.01	−4.257	23.74
0.8954	4.4915	48.10	−3.630	20.16
0.7302	3.6829	48.20	−2.993	19.98
0.6205	3.1478	48.17	−2.570	18.86
0.5247	2.6764	48.11	−2.197	17.50
0.4091	2.0992	48.08	−1.765	12.84
0.2668	1.3791	48.04	−1.161	12.23
0.1841	0.9529	48.18	−0.797	14.44
		HNO_3		
		10°C		
1.1115	3.7154	28.52	−4.517	−57.39
0.8581	2.8941	28.46	−3.652	−64.67
0.8112	2.7467	28.37	−3.473	−65.90
0.6142	2.0900	28.39	−2.745	−72.89
0.4714	1.6187	28.21	−2.164	−78.07
0.3427	1.1792	28.27	−1.615	−82.24
0.2279	0.7947	27.92	−1.102	−88.19
0.1116	0.3960	27.42	−0.553	−94.76
		25°C		
1.1115	3.5247	30.23		
1.1115	3.5219	30.26	−4.042	−31.84
0.85809	2.7420	30.22	−3.245	−37.07
0.81123	2.5963	30.22	−3.101	−38.62
0.61416	1.9797	30.18	−2.423	−43.11
0.47135	1.5271	30.15	−1.907	−46.75
0.34271	1.1170	30.08	−1.423	−50.90
0.22793	0.7466	30.02	−0.967	−54.43
0.11160	0.3681	29.91	−0.484	−58.32

Table 4.1 (continued)

m_2 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	${}^\phi V_2$ (cm^3 mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	${}^\phi C_{p,2}$ (J K^{-1}mol^{-1})
		40°C		
1.1115	3.3939	31.42	−3.766	−17.35
0.8581	2.6380	31.44	−3.040	−22.80
0.6142	1.9090	31.33	−2.280	−29.39
0.8112	2.4983	31.43	−2.896	−23.82
0.4714	1.4712	31.34	−1.800	−33.18
0.3427	1.0796	31.17	−1.341	−37.32
0.2279	0.7193	31.23	−0.912	−40.28
0.1116	0.3601	31.62	−0.458	−46.59
		55°C		
1.1115	3.3137	32.16	−3.615	−9.33
0.8581	2.5748	32.20	−2.928	−14.97
0.8112	2.4433	32.13	−2.788	−16.12
0.6142	1.8570	32.20	−2.206	−21.57
0.4714	1.4404	32.01	−1.748	−26.62
0.3427	1.0507	32.03	−1.289	−28.12
0.2279	0.7052	31.86	−0.883	−33.14
0.1116	0.3467	31.84	−0.441	−35.82
		H_2SO_4		
		10°C		
1.0127	6.3346	33.40	−2.282	41.45
0.7973	5.0601	32.94	−1.945	32.17
0.5635	3.6434	32.23	−1.503	20.24
0.4724	3.0807	31.88	−1.310	14.66
0.3780	2.4883	31.46	−1.080	9.69
0.2848	1.8987	30.82	−0.849	2.07
0.1781	1.2113	29.68	−0.557	−8.55
0.1035	0.7260	27.70	−0.337	−21.98

Table 4.1 (continued)

m_2 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	${}^\phi V_2$ (cm^3 mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	${}^\phi C_{p,2}$ (J K^{-1}mol^{-1})
		25°C		
1.0127	6.0224	36.35	−1.910	69.13
0.7973	4.8036	36.03	−1.567	64.97
0.5635	3.4508	35.53	−1.146	60.74
0.4724	2.9154	35.26	−0.967	59.32
0.3780	2.3537	34.91	−0.774	58.18
0.2848	1.7934	34.41	−0.574	57.71
0.1781	1.1403	33.56	−0.343	58.13
0.1035	0.6787	32.17	−0.185	58.61
		40°C		
1.0127	5.8017	38.41	−2.003	72.75
0.7973	4.6244	38.15	−1.615	70.33
0.5635	3.3318	37.77	−1.160	68.05
0.4724	2.8020	37.54	−0.965	68.19
0.3780	2.2583	37.32	−0.761	68.82
0.2848	1.7185	36.92	−0.551	70.75
0.1781	1.0923	36.13	−0.312	75.48
0.1035	0.6478	35.03	-0.151_0	83.57
		55°C		
1.0127	5.6816	39.48	−2.254	65.19
0.7973	4.5312	39.21	−1.802	63.37
0.5635	3.2432	38.98	−1.294	61.76
0.4724	2.7362	38.82	−1.084	61.50
0.3780	2.2208	38.51	−0.852	62.32
0.2848	1.6773	38.24	-0.621_6	64.61
0.1781	1.0629	37.66	-0.354_0	70.83
0.1035	0.6244	37.15	-0.169_7	83.72

Calculations on aqueous solutions containing sulphuric acid will be treated separately from those for the other simple acids. Because of calculations that follow in separate Chapters, it is appropriate to fit these data using expressions derived from the *extended* Debye-Hückel theory.

4.3.2 Extended Debye-Hückel terms

The extended Debye-Hückel theory (DEBYE and HÜCKEL, 1923) is better suited in some instances for the representation of the thermodynamic properties of aqueous electrolytes compared to the non-extended theory because of its improved applicability at higher ionic strengths. The extended Debye-Hückel theory can be written in terms of activity coefficients as (PITZER and BREWER, 1961)

$$\ln \gamma_{\pm} = -A_{\gamma}|z_{+}z_{-}|\frac{I^{1/2}}{1 + B_{\gamma}\mathring{a}I^{1/2}} \tag{4.7}$$

where all terms were defined in Chapter 2, except B_{γ}, which is defined by (ROBINSON and STOKES, 1959)

$$B_{\gamma} = \frac{1}{(DT)^{1/2}}\left(\frac{8\pi N_{o}e^{2}}{1000k}\right)^{1/2} \tag{4.8}$$

and å, which is an ion-size parameter. Another commonly used form of the extended Debye-Hückel equation is that due to GÜNTELBERG (1926):

$$\ln \gamma_{\pm} = -A_{\gamma}|z_{+}z_{-}|\frac{I^{1/2}}{1 + I^{1/2}} \tag{4.9}$$

where the å parameter is set equal to 3.04 Å at 25°C.

The relationships of the mean ionic activity coefficients of aqueous electrolyte solutions to other thermodynamic properties such as the partial molar volume and heat capacity were detailed in Chapter 2. It suffices to state here

$$\left(\frac{\partial \ln \gamma_{\pm}}{\partial p}\right)_{T} = \frac{\bar{V} - \bar{V}^{\circ}}{\nu RT} \tag{4.10}$$

and

$$\left(\frac{\partial^{2} \ln \gamma_{\pm}}{\partial T^{2}}\right)_{p} = \frac{\bar{C}_{p} - \bar{C}_{p}^{\circ}}{\nu RT^{2}} + 2\frac{\bar{H} - \bar{H}^{\circ}}{\nu RT^{3}} \tag{4.11}$$

where $[\partial(\bar{H} - \bar{H}^{\circ})/\partial T]_{p} = \bar{C}_{p} - \bar{C}_{p}^{\circ}$.

Differentiations of the extended Debye-Hückel expression with respect to pressure and twice with respect to temperature (as shown above) lead to expressions that

describe the limiting behaviour of volumes and heat capacities in dilute solutions. The equations that represent the partial molar properties in very dilute solution are similar to those in Chapter 2 except now the extended form of the Debye-Hückel equation (as modidifed by GÜNTELBERG) replaces the other more simple limiting law

$$\bar{Y} = \bar{Y}^\circ + \bar{A}_Y \omega \frac{I^{1/2}}{1 + I^{1/2}} \tag{4.12}$$

The expressions that result from the extended Debye-Hückel theory for the corresponding *apparent* molar properties are slightly more complicated because of the relationship between apparent and partial molar properties:

$$\bar{Y} = {}^{\phi}Y + I\left(\frac{\partial {}^{\phi}Y}{\partial I}\right)_{T,p} \tag{4.13}$$

Multiplying eq. 4.13 by dI and integrating leads to

$$\int_0^I \bar{Y}\,dI = \int_0^I {}^{\phi}Y\,dI + \int_0^I I\,d^{\phi}Y \tag{4.14}$$

Consideration of eq. 4.12 or the first term in eq. 4.14, shows that this term describes the limiting law behaviour.

$$\int_0^I \bar{Y}\,dI = \int_0^I \left(\bar{Y}^\circ + \bar{A}_Y \omega \frac{I^{1/2}}{1 + I^{1/2}}\right) dI \tag{4.15}$$

This integral can be evaluated by making the substitution $x = 1 + I^{1/2}$

$$\int_0^I \frac{I^{1/2}}{1 + I^{1/2}} dI = 2\int_1^x \frac{(x-1)^2}{x} dx \tag{4.16}$$

Term by term integration and substitution of $x = 1 + I^{1/2}$ (with change in the limits of integration) leads to

$$\int_0^I \frac{I^{1/2}}{1 + I^{1/2}} dI = I - 2I^{1/2} + 2\ln(1 + I^{1/2}) \tag{4.17}$$

Noting that $\bar{Y}^\circ$ is independent of ionic strength, and that the integral in $d^{\phi}Y$ can be evaluated using the integration by parts method

$$\int_{{}^{\phi}Y^\circ}^{{}^{\phi}Y} I\,d^{\phi}Y = I^{\phi}Y - \int_0^I {}^{\phi}Y\,dI \tag{4.18}$$

Combination and rearrangement of eqs. 4.14, 4.17, and 4.18 leads to the desired expression

$${}^{\phi}Y = \bar{Y}^\circ + \frac{\omega \bar{A}_Y}{I}\left[I - 2I^{1/2} + 2\ln(1 + I^{1/2})\right] \tag{4.19}$$

where it should again be noted that $\bar{A}_Y$ is the Debye-Hückel limiting slope for *partial* molar properties, and that the slope for apparent molar properties is related by $A_Y = \frac{2}{3}\bar{A}_Y$.

The extended Debye-Hückel equation (shown above in eq. 4.19) is normally written in a slightly different form (PITZER and BREWER, 1961). Even though the above form is more compact and more easily equated to ionic strength effects, the more familiar form described below will be used throughout the rest of this thesis.

4.3.3 $HClO_4$ and HNO_3

The functional dependence of the apparent molar volumes and heat capacities of $HClO_4$ and HNO_3 are well represented by extended Debye-Hückel equations as described in the preceding section.

$$^{\phi}Y_2 = \bar{Y}_2^{\circ} + \frac{3}{2}\omega A_Y \left(\frac{1}{\Lambda} - \frac{\sigma}{3}\right) I^{1/2} + B_Y I + C_Y I^{3/2} \tag{4.20}$$

where

$$I = \omega m = \frac{1}{2}\sum m_i z_i^2 \tag{4.21}$$

$$\Lambda = 1 + I^{1/2} \tag{4.22}$$

$$\sigma = \frac{3\left(\Lambda - \frac{1}{\Lambda} - 2\ln\Lambda\right)}{I^{3/2}} \tag{4.23}$$

Values for the Debye-Hückel limiting slopes (A_Y) were taken from ANANTHASWAMY and ATKINSON (1984) and are listed in Table 4.2.

Equation 4.20 was fitted to the experimental apparent molar properties listed in Table 4.1 to generate the values of $\bar{Y}_2^{\circ}$, B_Y, and C_Y for nitric and perchloric acid that are listed in Table 4.3. It was found that the temperature dependence of the B_Y and C_Y parameters for perchloric acid could be satisfactorily represented by equations of the form

$$B_Y(\text{and } C_Y) = p_1 + \frac{p_2}{T} + p_3 T + p_4 T^2 \tag{4.24}$$

using only three of the four parameters without significant loss in the precision of the data fits. The p_i parameters are fitting coefficients and T is the temperature in kelvins. We have subsequently refit the data listed in Table 4.1 using the constrained fits to the B and C parameters.

Table 4.2: Density, specific heat capacity, and Debye-Hückel slopes for water at 10, 25, 40, and 55°C from KELL (1967, 1972) and ANANTHASWAMY and ATKINSON (1984), respectively.

t (°C)	d_1° (g cm^{-3})	$c_{p,1}^\circ$ (J K^{-1}g^{-1})	A_V (cm^{3}kg$^{1/2}$mol$^{-3/2}$)	A_C (J kg$^{1/2}$mol$^{-3/2}$K^{-1})
10	0.999700	4.1919	1.6420	28.446
25	0.997047	4.1793	1.8743	32.783
40	0.992219	4.1783	2.1540	37.446
55	0.985695	4.1821	2.4946	42.699

Application of eq. 4.24 to the B and C parameters obtained from fits to data for nitric acid were found to increase the overall standard deviation of the fit and thus was not used for determining the standard state values. These fits are included in Table 4.3 that are to be used for *interpolation purposes only.*

Plots of ${}^{\phi}Y_2$ minus the Debye-Hückel limiting law (eq. 4.20) are shown in Figures 4.1 and 4.2 for perchloric acid and Figures 4.3 and 4.4 for nitric acid. The ability of the above described procedure to represent the high concentration properties and the standard state values (infinite dilution) is also illustrated in these plots.

4.3.4 H_2SO_4–prelude

Aqueous solutions containing sulphuric acid are comprised primarily of (H^+, HSO_4^-) although there are also appreciable amounts of sulphate ion. The single equilibrium that describes the speciation of sulphuric acid solutions is represented by eq. 4.25.

$$HSO_4^-(aq) = H^+(aq) + SO_4^{2-}(aq) \tag{4.25}$$

The measurements that lead to "experimental" apparent molar volumes and heat capacities that were reported in Table 4.1 for aqueous solutions containing sulphuric acid must be treated taking into account the changing relative amounts of sulphate and bisulphate ions.

Most of the equilibrium data for this reaction near room temperature (5 to 55°C) were analyzed by PITZER *et al.* (1977) in a comprehensive treatment of many thermodynamic properties for this system (activities, enthalpies of dilution, etc.). Accurate speciation calculations at room temperature are therefore accessible for this reaction. The apparent molar volumes and heat capacities that were reported in Table 4.1 were calculated from the stoichiometric molalities using eq. 4.4. These "experimental" apparent molar volumes can be written in terms of all of the species present at equilibrium

$${}^{\phi}Y^{exp} = (1-\alpha){}^{\phi}Y(H^+, HSO_4^-) + \alpha{}^{\phi}Y(2H^+, SO_4^{2-}) \tag{4.26}$$

The apparent molar heat capacities of these solutions, besides containing contributions from the individual ionic species, also contain contributions due to "chemical relaxation". Since the effects of chemical relaxation are discussed in several of the

Table 4.3: Standard state partial molar volumes, heat capacities, and ionic strength parameters for solutions of HNO_3 and $HClO_4$ from 10 to 55°C.

t (°C)	${}^{\phi}V_2^{\circ}$ ($cm^3 mol^{-1}$)	B_V ($cm^3 kg\ mol^{-2}$)
	$HClO_4$*	
10	41.63 ± 0.04	-0.0353 ± 0.06
25	44.04 ± 0.02	-0.4601 ± 0.04
40	46.24 ± 0.03	-0.5855 ± 0.04
55	47.31 ± 0.05	-0.6627 ± 0.07
	HNO_3	
10	27.43 ± 0.08	0.1175 ± 0.11
25	29.41 ± 0.01	-0.2592 ± 0.01
40	30.47 ± 0.05	-0.2912 ± 0.07
55	31.14 ± 0.05	-0.4196 ± 0.07

Table 4.3: (continued)

t (°C)	${}^{\phi}C^{\circ}_{p,2}$ ($JK^{-1}mol^{-1}$)	B_C (J kg $K^{-1}mol^{-2}$)	C_C (J $kg^{3/2}K^{-1}mol^{-5/2}$)
		$HClO_4$*	
10	-62.2 ± 0.7	47.01 ± 3.7	-17.18 ± 3.2
25	-25.0 ± 0.1	17.35 ± 2.8	-3.868 ± 2.6
40	-9.0 ± 1.0	3.75 ± 5.7	1.42 ± 4.9
55	-5.2 ± 2.0	4.65 ± 20	-0.54 ± 16
		HNO_3	
10	-106.4 ± 0.6	41.29 ± 3.4	-11.91 ± 3.0
25	-69.0 ± 0.5	13.57 ± 2.9	2.321 ± 2.6
40	-58.3 ± 0.7	18.18 ± 4.0	-1.27 ± 3.5
55	-48.0 ± 1.3	-4.245 ± 7.9	15.74 ± 6.9

* reported uncertainties were those derived from the fits with unconstrained values of the B_Y and C_Y parameters.

For $HClO_4$ calculations from 10 to 55°C use:
$B_V = -38.635 + 8170.9/T + 0.00012152T^2$
$B_C = -3150.1 + 671750/T + 0.010287T^2$
$C_C = 1578.4 - 332590/T - 0.0052506T^2$

For HNO_3 interpolations between experimental temperatures from 10 to 55°C use:
$B_V = 28.554 - 0.17778T + 0.0002729T^2$
$B_C = 893.55 - 4.8662T + 0.006521T^2$
$C_C = 123.54 - 1.3352T + 0.0030499T^2$

$T/K = t/°C + 273.15$

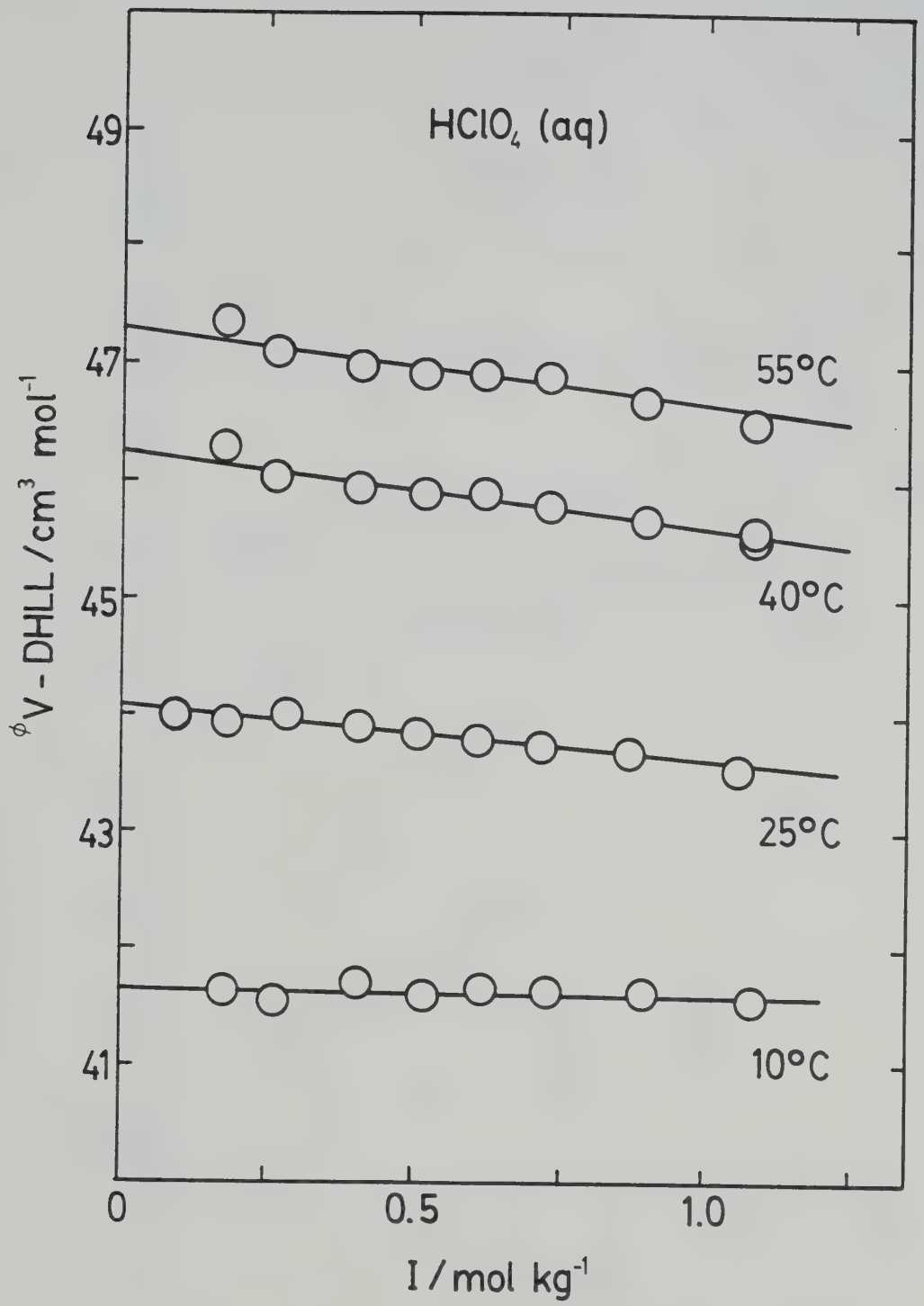

Figure 4.1: ${}^{\phi}V$ minus the extended Debye-Hückel limiting law (DHLL) for aqueous $HClO_4$ from 10 to 55°C versus ionic strength. Lines are least squares fits of eq. 4.20

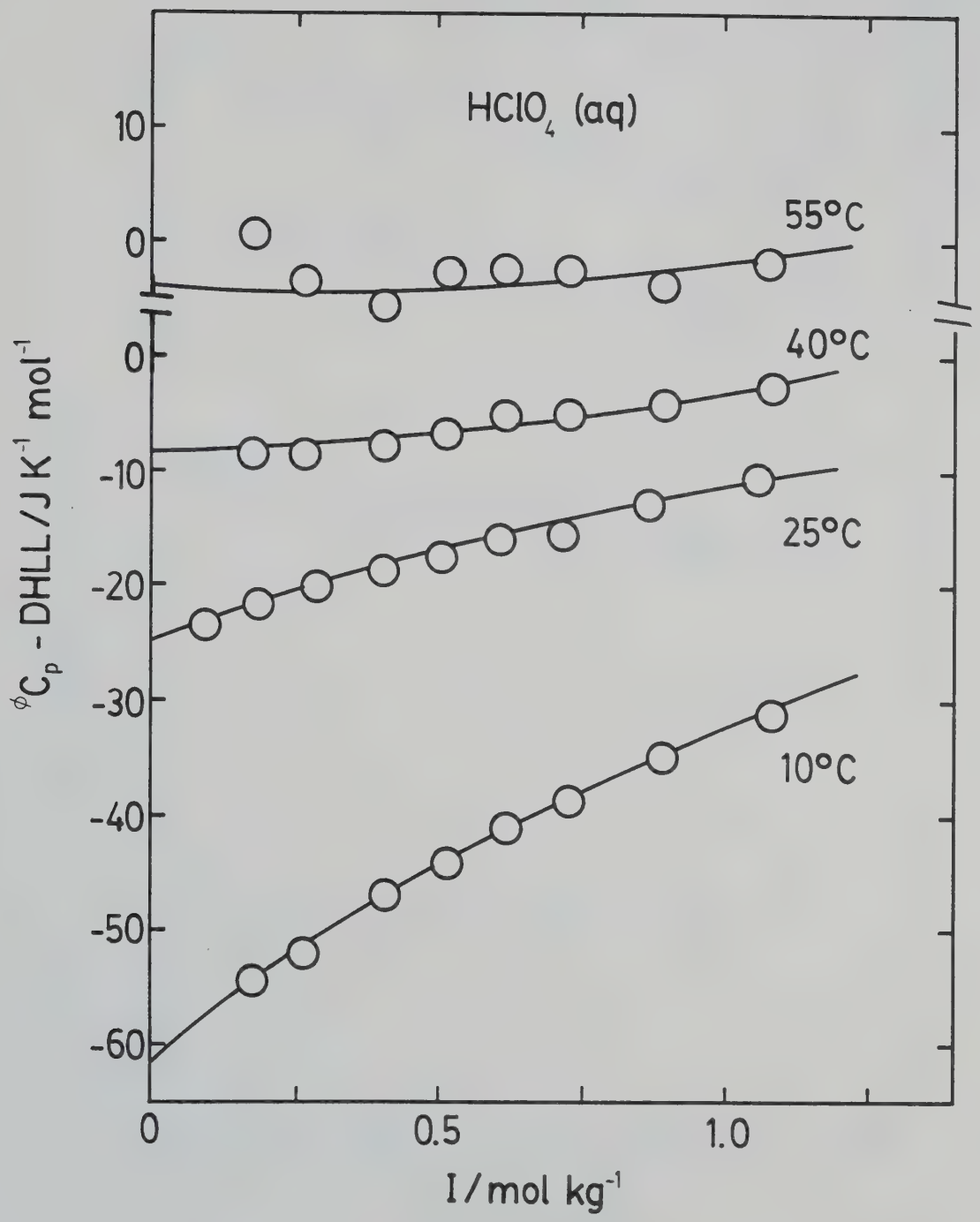

Figure 4.2: ${}^{\phi}C_p$ minus the extended Debye-Hückel limiting law (DHLL) for aqueous $HClO_4$ from 10 to 55°C versus ionic strength. Lines are least squares fits of eq. 4.20

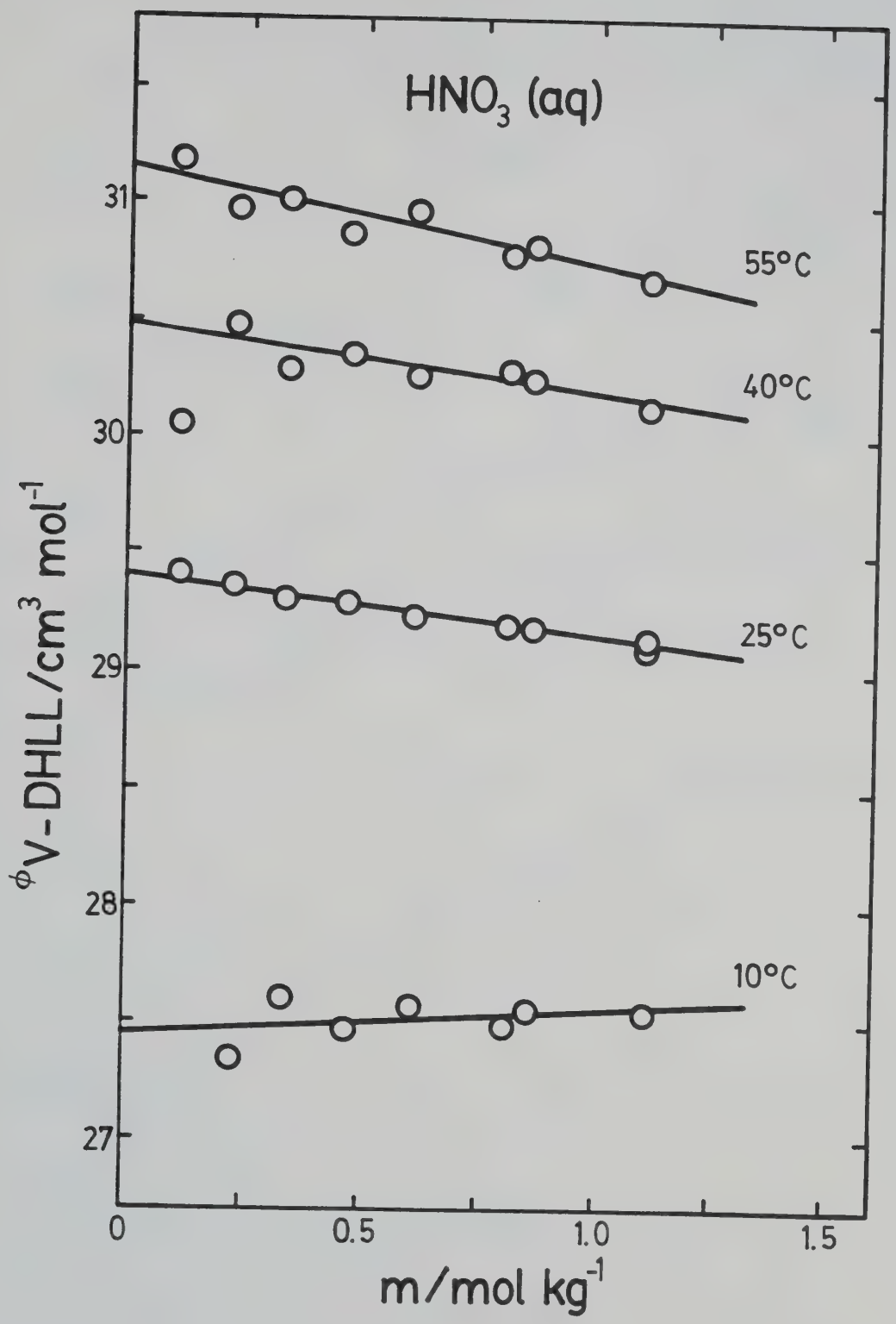

Figure 4.3: ${}^{\phi}V$ minus the extended Debye-Hückel limiting law (DHLL) for aqueous HNO_3 from 10 to 55°C versus ionic strength. Lines are least squares fits of eq. 4.20

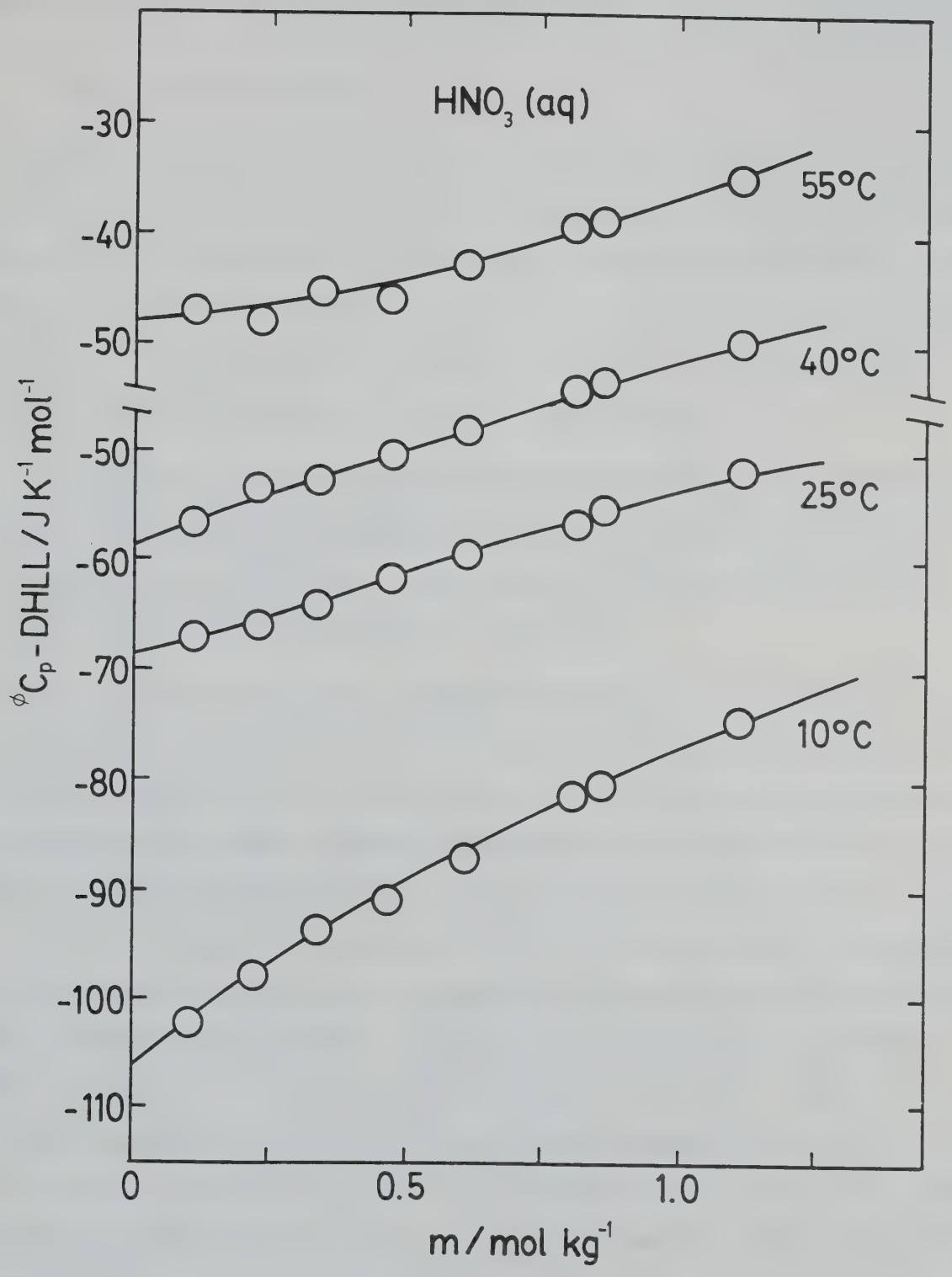

Figure 4.4: ${}^{\phi}C_p$ minus the extended Debye-Hückel limiting law (DHLL) for aqueous HNO_3 from 10 to 55°C versus ionic strength. Lines are least squares fits of eq. 4.20

following Chapters, an account of the general method and the development of several equations will be presented here for sulphuric acid.

4.3.5 Chemical Relaxation

Heat capacity measurements on aqueous solutions containing partially dissociated solutes that date from as far back as 1941 (RANDALL and TAYLOR, 1941), showed peculiar trends in the observed specific heat as a function of ionic strength. For heat capacity measurements on sulphuric acid, increasing apparent molar heat capacities from about 0.2 to 0.05 molal were observed, contrary to that expected for totally dissociated solutes. RANDALL and TAYLOR (1941) stated:

> If a reaction,–for example, the dissociation of bisulfate ion into hydrogen and sulfate ions,–is more complete at a higher temperature than at a lower, then the heat corresponding to the additional fraction of bisulfate ion dissociated at the higher temperature will be measured as though it were a part of the heat capacity of the solution.

This is one of the earliest direct statements regarding the contributions that are presently labeled "chemical relaxation". However, it turns out that this effect is not limited to reactions that are more complete at higher temperatures (endothermic)[1] but also those that are less complete (exothermic) as will be shown following.

The most comprehensive accounts of the contributions of "chemical relaxation" were produced by Hepler and colleagues (WOOLLEY and HEPLER, 1977; MAINS *et al.*, 1984) as impetus from precise calorimetric measurements with flow calorimeters. Slightly different (but equivalent) approaches were outlined by JOLICOEUR *et al.* (1979), PITZER *et al.* (1977), and BLANDAMER *et al.* (1984). Some of the more subtle aspects of these calculations have also been discussed (BARBERO *et al.*, 1983).

The effect of chemical relaxation on heat capacities can be visualized by expressing the total enthalpy of a system (containing solvent, solute, and products obtained from dissociation or polymerization of the solute) as:

$$H = \sum_k n_k H_k \tag{4.27}$$

[1] It was known at the time from the accurate measurements of PITZER (1937) that the enthalpy of this reaction was exothermic and equal to –5.2 kcal mol^{-1}.

where n_k and H_k are the numbers of moles and partial molar enthalpies of each component in the system. Equation 4.27 can be differentiated with respect to temperature at constant pressure to yield

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \sum_k n_k \left(\frac{\partial H_k}{\partial T}\right)_p + \sum_k H_k \left(\frac{\partial n_k}{\partial T}\right)_p \tag{4.28}$$

For systems that do not undergo any change in relative concentrations of components, the only contribution to the heat capacities are those arising from the first term in eq. 4.28. However, for many other systems, from those consisting of a liquid in equilibrium with its vapour, or solutes present in aqueous solution, the total heat capacity is due to all species present (1st term) and also to the change in the number of moles of each species present (2nd term).

It is convenient to discuss chemical relaxation in terms of the fractional extent of a reaction and its relation to apparent molar properties. Following WOOLLEY and HEPLER (1977), the heat capacity of a solution containing one kilogram of water and any solutes can be expressed by

$$C_p(sol) = \left(\frac{\partial H}{\partial T}\right)_p^{sp} + \left(\frac{\partial H}{\partial T}\right)_p^{rel} \tag{4.29}$$

where *sp* represents "species" or solutes and *rel* represents the contribution from chemical relaxation. Since the "experimental" apparent molar heat capacity is calculated from expressions similar to eq. 4.4, the following equation results:

$${}^{\phi}C_p^{exp} = \frac{C_p(sol) - C_p(wat)}{m} \tag{4.30}$$

where $C_p(sol)$ and $C_p(wat)$ are the heat capacities (per kilogram) of solution and water, respectively. Combination of eq. 4.30 with eq. 4.29 leads to

$${}^{\phi}C_p^{exp} = \frac{\left[\left(\frac{\partial H}{\partial T}\right)_p^{sp} + \left(\frac{\partial H}{\partial T}\right)_p^{rel} - C_p(wat)\right]}{m} \tag{4.31}$$

Since the heat capacity of solutions containing non-dissociating solutes contain no contributions from chemical relaxation, the desired apparent molar heat capacity of the species (*sp*) from solutions containing partially dissociated solutes can be calculated using

$${}^{\phi}C_p = {}^{\phi}C_p^{exp} - \frac{\left(\frac{\partial H}{\partial T}\right)_p^{rel}}{m} \tag{4.32}$$

This last term in eq. 4.32 is the relaxation term that must be carefully evaluated in order to account for chemical relaxation.

As done by WOOLLEY and HEPLER (1977), the relaxation term can be written

$$\left(\frac{\partial H}{\partial T}\right)_p^{rel} = \left(\frac{\partial H^{rel}}{\partial \alpha m}\right)_p \times \left(\frac{\partial \alpha m}{\partial T}\right)_p \tag{4.33}$$

where α represents the fractional extent of reaction. The quantity $(\partial H/\partial \alpha m)_p$ is directly related to the enthalpy of reaction

$$\left(\frac{\partial H^{rel}}{\partial \alpha m}\right)_p = \Delta H_{rxn} \tag{4.34}$$

where ΔH_{rxn} corresponds to the enthalpy of the reaction at the ionic strength of interest. Substituting this expression into eq. 4.33 and combining with eq. 4.32 leads an expression for the contribution of chemical relaxation to *apparent* molar heat capacities[2]

$${}^{\phi}C_p = {}^{\phi}C_p^{exp} - \Delta H_{rxn}\left(\frac{\partial \alpha}{\partial T}\right)_p \tag{4.35}$$

Of present concern is the evaluation of the contribution of chemical relaxation to measured heat capacities of solutions containing bisulphate and sulphate ions. The equilibrium reaction equation and the equilibrium molalities in terms of α and the stoichiometric molality m are given below.

$$\begin{array}{ccccc} HSO_4^-(aq) & = & H^+(aq) & + & SO_4^{2-}(aq) \\ (1-\alpha)m & & (1+\alpha)m & & \alpha m \end{array} \tag{4.36}$$

The equilbrium constant is defined in terms of m, α, and activity coefficients by

$$K = \frac{\alpha m(1+\alpha)}{1-\alpha}\frac{\gamma_{H^+}\gamma_{SO_4^{2-}}}{\gamma_{HSO_4^-}} \tag{4.37}$$

---

[2]Note that in eq. 4.35, the quantity $(\partial \alpha/\partial T)_p$ is not specified as being at constant molality as in various previous works (BARBERO *et al.*, 1983) since molality is constant as a direct result of the nature of this quantity. Derivation of eq. 4.35 would not be possible if molality were not constant. In the past some confusion has arisen concerning constant molality and ionic strength. In this work on sulphuric acid solutions, and indeed in all works, the molality is constant although the ionic strength normally changes. Relationships between thermodynamic properties such as enthalpies of dilution pertaining to systems with a changing equilibrium must be carefully related to derivatives of activity coefficients with temperature at constant molality (experimental) and constant composition (constant ionic strength).

The equilibrium speciation is readily obtained by rearranging and solving eq. 4.37, using the quadratic formula and expressions for K and $(\gamma_{H^+}\gamma_{SO_4^{2-}}/\gamma_{HSO_4^-})$ from PITZER *et al.* (1977). As mentioned previously, PITZER *et al.* (1977) have treated most low temperature thermodynamic data for aqueous sulphuric acid solutions in terms of the Pitzer ion interaction model (discussed in detail for other systems in Chapters 7 and 16). This analysis will be relied upon almost entirely for calculations involving speciation and relaxation for the solutions under present investigation.

The activity coefficient ratio for this equilibrium $(\gamma_{H^+}\gamma_{SO_4^{2-}}/\gamma_{HSO_4^-})$, that is denoted by γ_r (r =ratio), has the form (PITZER *et al.*, 1977)

$$\begin{aligned}\ln\gamma_r &= 4f^\gamma - 4\alpha m B_{H1} + 2m(1+2\alpha)\beta_{H2}^{(0)} + 2m^2(1+\alpha)(1+3\alpha)C_{H2} + \\ &\quad 4m^2(1-\alpha^2)B_{H1'} \qquad (4.38)\end{aligned}$$

in which various symbols are defined by

$$f^\gamma = -A_\phi\left[\frac{I^{1/2}}{1+1.2I^{1/2}} + \frac{2\ln(1+1.2I^{1/2})}{1.2}\right] \qquad (4.39)$$

$$B_{H1} = \beta_{H1}^{(0)} + \frac{\beta_{H1}^{(1)}[1-(1+2I^{1/2})\exp(-2I^{1/2})]}{2I} \qquad (4.40)$$

$$B_{H1'} = \frac{\beta_{H1}^{(1)}[-1+(1+2I^{1/2}+2I)\exp(-2I^{1/2})]}{2I^2} \qquad (4.41)$$

Here $\beta_{H1}^{(0)}$, $\beta_{H1}^{(1)}$, $\beta_{H2}^{(0)}$, and $C_{H2} = C_{H2}^{\phi}/2^{3/2}$ are all constants independent of ionic strength but dependent on temperature as given by the following equations:

$$\beta_{H1}^{(0)} = 0.05584 + \frac{46.040}{T} \qquad (4.42)$$

$$\beta_{H1}^{(1)} = -0.65758 + \frac{336.514}{T} \qquad (4.43)$$

$$\beta_{H2}^{(0)} = -0.32806 + \frac{98.607}{T} \qquad (4.44)$$

$$C_{H2}^{\phi} = 0.25333 - \frac{63.124}{T} \qquad (4.45)$$

The equilibrium constant for the reaction represented by eq. 4.36 is given by

$$\ln K = -14.0321 + \frac{2825.2}{T} \qquad (4.46)$$

Differention of eq. 4.37 and subsequent rearrangement leads to

$$\left(\frac{\partial\alpha}{\partial T}\right)_p = \frac{\frac{K\Delta H^\circ(1-\alpha)}{RT^2} - \alpha m(1+\alpha)\gamma_r\left(\frac{\partial\ln\gamma_r}{\partial T}\right)_p}{m\gamma_r(1+2\alpha)+K} \qquad (4.47)$$

As can be seen in the preceding equation, knowledge of γ_r as a function of temperature can be conveniently taken from differentiated versions of eqs. 4.38-4.45 listed above.

A special note is required concerning the evaluation of the temperature derivatives of those properties contained in eq. 4.38 that are dependent both on ionic strength and temperature. The following point holds for all calculations of chemical relaxation and is worth considering in detail. The quantities represented by f^{γ}, B_{H1}, and $B_{H1'}$ are all functions of both ionic strength and temperature. Evaluation of derivatives at constant pressure is required, which leads to the total differential of these general types of quantities denoted by g:

$$g = g(I, T, p) \tag{4.48}$$

$$dg = \left(\frac{\partial g}{\partial I}\right)_{T,p} dI + \left(\frac{\partial g}{\partial T}\right)_{I,p} dT + \left(\frac{\partial g}{\partial p}\right)_{T,I} dp \tag{4.49}$$

Because pressure is constant, the last term in eq. 4.49 is equal to zero. Dividing through by dT and imposing constant pressure leads to

$$\left(\frac{\partial g}{\partial T}\right)_p = \left(\frac{\partial g}{\partial I}\right)_{T,p} \left(\frac{\partial I}{\partial T}\right)_p + \left(\frac{\partial g}{\partial T}\right)_{I,p} \tag{4.50}$$

Since the ionic strength in solutions of aqueous sulphuric acid is given by

$$I = m(1 + 2\alpha) \tag{4.51}$$

eq. 4.50 can be simplified to

$$\left(\frac{\partial g}{\partial T}\right)_p = 2m \left(\frac{\partial \alpha}{\partial T}\right)_p \left(\frac{\partial g}{\partial I}\right)_{T,p} + \left(\frac{\partial g}{\partial T}\right)_{I,p} \tag{4.52}$$

It should be noted that eqs. 4.48-4.50 are general, and must be considered in any analysis of chemical relaxation.

The differentiated version of eq. 4.38 obtained by consideration of the ionic strength and temperature dependence of certain quantities as shown in eq. 4.52, can be combined with eq. 4.47, and after considerable rearrangement, the final expression for $(\partial\alpha/\partial T)_p$ is

$$\left(\frac{\partial \alpha}{\partial T}\right)_p \left\{ m\gamma_r(1 + 2\alpha) + K + \alpha m(1 + \alpha)\gamma_r \left[8m \left(\frac{\partial f^{\gamma}}{\partial I}\right)_{p,T} - 4B_{H1}m - 8\alpha m^2 \left(\frac{\partial B_{H1}}{\partial I}\right)_{p,T} \right.\right.$$

$$+4m\beta_{H2}^{(0)} + 4(2+3\alpha)m^2 C_{H2} - 8m^2\alpha B_{H1'} + 8m^3(1-\alpha^2)\left(\frac{\partial B_{H1'}}{\partial I}\right)_{p,T}\Bigg]\Bigg\} =$$

$$\frac{K\Delta H^\circ(1-\alpha)}{RT^2} - \gamma_r\alpha m(1+\alpha)\left[4\left(\frac{\partial f^\gamma}{\partial T}\right)_{p,I} - 4\alpha m\left(\frac{\partial B_{H1}}{\partial T}\right)_{p,I} + 2m(1+2\alpha)\left(\frac{\partial \beta_{H2}^{(0)}}{\partial T}\right)_{p,I}\right.$$

$$\left. +2(1+\alpha)(1+3\alpha)m^2\left(\frac{\partial C_{H2}}{\partial T}\right)_{p,I} + 4m^2(1-\alpha^2)\left(\frac{\partial B_{H1'}}{\partial T}\right)_{p,I}\right] \qquad (4.53)$$

This expression (eq. 4.53) was used to evaluate relaxation contributions to the measured heat capacities. For systems that do not have such complete relationships of equilibrium constants, activity coefficients, and related parameters, these calculations become significantly more complex. The temperature dependence of activity coefficients are related to relative partial molar enthalpies of dilution by

$$\left(\frac{\partial \ln \gamma_\pm}{\partial I}\right)_{const.\ comp.} = -\frac{\bar{L}_\pm}{\nu RT^2} \qquad (4.54)$$

Derivation of appropriate expressions using this relationship can be difficult (BARBERO *et al.*, 1983). The temperature dependence of stoichiometric activity coefficients for systems such as sulphuric acid or some other partially ionized solute relate to the *total* enthalpies of dilution (not constant composition) and thus also must be analyzed in terms of the total differential to extract information for the desired "species" (*sp*).

It is worth considering the sign of chemical relaxation corrections in a general sense. If the quantity $(\partial\alpha/\partial T)_p$ is positive, this implies that the enthalpy of the reaction is endothermic (increasing dissociation with increasing temperature). Accordingly, if $(\partial\alpha/\partial T)_p$ is negative then the enthalpy of reaction must be exothermic. Since the relaxation contribution is evaluated by the product of the enthalpy change and $(\partial\alpha/\partial T)_p$, the contribution is *always* positive.

4.3.6 H_2SO_4–calculations

As shown in eq. 4.26, and described in the preceding section, the experimental apparent molar volumes and heat capacities can be expressed in terms of the stoichiometric molalities and the fractional extents of reaction (α) by

$${}^\phi V^{exp} = (1-\alpha)\,{}^\phi V(\mathrm{H^+},\ \mathrm{HSO_4^-}) + \alpha\,{}^\phi V(2\mathrm{H^+},\ \mathrm{SO_4^{2-}}) \qquad (4.55)$$

and

$$^{\phi}C_p^{exp} = (1-\alpha)^{\phi}C_p(\mathrm{H^+},\ \mathrm{HSO_4^-}) + \alpha^{\phi}C_p(2\mathrm{H^+},\ \mathrm{SO_4^{2-}}) + {}^{\phi}C_p^{rel} \tag{4.56}$$

Since there are appreciable amounts of solute that can be considered to exist as $(2\mathrm{H^+},\ \mathrm{SO_4^{2-}})$, apparent molar volume and heat capacity data for this species must be subtracted from the total "experimental" quantites to yield desired properties of $\mathrm{HSO_4^-}$(aq). This combination of ions has been estimated from two different schemes, the first only at 25°C, and the second for all other temperatures:

$$\begin{aligned} 25°\mathrm{C}: \ {}^{\phi}Y(2\mathrm{H^+},\ \mathrm{SO_4^{2-}}) &= {}^{\phi}Y(2\mathrm{K^+},\ \mathrm{SO_4^{2-}}) - 2^{\phi}Y(\mathrm{K^+},\ \mathrm{Cl^-}) + \\ &\quad 2^{\phi}Y(\mathrm{H^+},\ \mathrm{Cl^-}) \end{aligned} \tag{4.57}$$

$$\begin{aligned} 10-55°\mathrm{C}: \ {}^{\phi}Y(2\mathrm{H^+},\ \mathrm{SO_4^{2-}}) &= {}^{\phi}Y(2\mathrm{Na^+},\ \mathrm{SO_4^{2-}}) - 2^{\phi}Y(\mathrm{Na^+},\ \mathrm{Cl^-}) + \\ &\quad 2^{\phi}Y(\mathrm{H^+},\ \mathrm{Cl^-}) \end{aligned} \tag{4.58}$$

Volumetric and heat capacity expressions of the general type corresponding to fits of non-extended Debye-Hückel equations to experimental data for $\mathrm{K_2SO_4}$ at 25°C were taken from Chapter 2. Heat capacity expressions were taken directly from DESNOYERS *et al.* (1976) for KCl and HCl. The apparent molar volume data from FORTIER *et al.* (1974) were refit using these same general class of expressions, and finally volumetric data for HCl were taken from ALLRED and WOOLLEY (1981). Volumetric data for NaCl and $\mathrm{Na_2SO_4}$ were calculated from the parameters in CONNAUGHTON *et al.* (1986). For HCl the values from ALLRED and WOOLLEY (1981) were used at 10 and 40°C, and the expression from HERRINGTON *et al.* (1985) was used at 55°C. Heat capacity expressions applicable at 10, 40, and 55°C for NaCl were derived from PITZER *et al.* (1984), for HCl from Tremaine et al. (1986), and for $\mathrm{Na_2SO_4}$ from ROGERS and PITZER (1981).

The speciations of all of these solutions were calculated as outlined in the previous section. The relaxation corrections were calculated using the data above, with the standard state enthalpy of reaction coming from PITZER *et al.* (1977), also as outlined in the previous section. The standard state enthalpy change ($\Delta H° = -23.49$ kJ mol^{-1}) can be derived from Pitzer's $\ln K$ expression ($\ln K = -14.0321 + 2825.2/T$). This result is in fair to good agreement with direct calorimetric results of PITZER (1937), –21.8 kJ mol^{-1}, AUSTIN and MAIR (1962), –23.8 kJ mol^{-1},

CHRISTENSEN *et al.* (1966), − − 23.4, − − 17.2 kJ mol^{-1}, and IZATT *et al.* (1969), − − 20.5 kJ mol^{-1}. Values of the standard state enthalpy change that can be calculated from the temperature dependence of the equilibrium constants range from –9 to –23.4 kJ mol^{-1} (HAMER, 1934; YOUNG *et al.*, 1978; NAIR and NANCOLLAS, 1958; FLETCHER, 1964; MARSHALL and JONES, 1966; LIETZKE *et al.*, 1961; DAWSON *et al.*, 1986).

The calculations of speciation were performed iteratively by first assuming that all activity coefficients were unity, and going through cycles of calculating speciation, ionic strength, activity coefficients, etc. The α values were found to converge quickly. From these calculated α values and the equations given in the preceding section, the relaxation contributions were calculated. The enthalpies of reaction required in such calculations are those at the ionic strength of the solution at the mean temperature of the calorimetric results. These $\Delta H^{\dagger}$ values were calculated from

$$\Delta H^{\dagger} = \Delta H^{\circ} - RT^2 \left(\frac{\partial \ln \gamma_r}{\partial T} \right)_p \tag{4.59}$$

The resulting data for the desired combination of ions H^+, HSO_4^- were well behaved in terms of the apparent molar volumes (typical shape of plots of the type shown in Figures 4.1 and 4.3). The shape of plots of the apparent molar heat capacity minus the Debye-Hückel limiting law against ionic strength showed typical behaviour at 25°C, but uncharacteristic behaviour at the other temperatures. It appeared that the assessed relaxational contributions to the heat capacities were too large (especially at low ionic strengths) at temperatures below 25°C, and too small above 25°C. As is evident from the comparison of the enthalpies associated with the bisulphate-sulphate equilibrium, the enthalpy value from PITZER *et al.* (1977) is slightly low but still reasonable. However, the temperature dependence of the enthalpy, that cannot be assessed from the equation used by PITZER *et al.* (1977) because of the zero value of the second derivative, must be considered for a proper analysis of speciation at temperatures other than 25°C. The results obtained from the procedure described above for 25° lead to standard state heat capacities and volumes for $H[HSO_4](aq)$. The change in standard state heat capacity for the bisulphate dissociation reaction was then calculated from data for K_2SO_4, KCl, and HCl as described previously. This led to a standard state heat capacity change of

-264.5 J $K^{-1}mol^{-1}$ for the reaction represented by eq. 4.25. As can be seen the large heat capacity change for this reaction means that the standard state enthalpy is not constant. Combination of the equilibrium expression from PITZER *et al.* (1977) with the presently derived heat capacity change at 25°C, leads to the expression

$$\ln K = -4.5563 + 2825.2\left(\frac{1}{T} - \frac{1}{298.15}\right) - 31.81\left[\ln\left(\frac{T}{298.15}\right) - 1 + \left(\frac{298.15}{T}\right)\right] \quad (4.60)$$

Results of speciation calculations with these "improved" temperature dependent equilibrium constants are given in Table 4.4. This expression is intended only for these calculations. A more rigorous equation can be derived from results for other temperatures other than 25°C as presented later for this same temperature range.

The introduction of the heat capacity term in the equilibrium constant for the bisulphate ion ionization reaction introduces a slight inconsistency in the treatment presented by PITZER *et al.* (1977) because the data used in this study did not warrant inclusion of a temperature dependent enthalpy. This will have negligible effect on our calculations of speciation and will have no effect upon extrapolation to infinite dilution of the apparent molar properties. However, because of the temperature dependence of several parameters required for relaxation calculations, the introduction of the ΔC_p term may have larger consequences here. A further analysis of the effect of this over the temperature range from 10 to 55° is not justified here. It is apparent, however, that a detailed review of all thermodynamic properties of sulphuric acid from 0 to 350°C should be written. Plans for such a review are in progress.[3] The results of all of the relaxation and speciation calculations are also given in Table 4.4.

Application of the extended Debye-Hückel equation (4.20) to the "experimental" apparent molar volumes listed in Table 4.1, and the apparent molar heat capacities listed in Table 4.4, has resulted in definition of the standard state partial molar volumes, heat capacities, and concentration dependent terms. It was found that simple polynomial fits did not represent the concentration dependent parameters well enough to warrant more constrained fits for refinement of the standard state

[3] J.K. Hovey and L.G. Hepler, in preparation

Table 4.4: Equilibrium speciation and ionic strengths in sulphuric acid solutions from PITZER *et al.* (1977).

m_2 (mol kg^{-1})	α	$(1-\alpha)m_2$ (mol kg^{-1})	αm_2 (mol kg^{-1})	I (mol kg^{-1})	${}^{\phi}C_p^{rel}$ (J K^{-1}mol^{-1})	${}^{\phi}C_p^{exp} - {}^{\phi}C_p^{rel}$ (J K^{-1}mol^{-1})
			10°C			
1.01265	0.33102	0.67744	0.33521	1.6830	152.06	−110.61
0.79727	0.31694	0.54459	0.25268	1.3026	140.59	−108.42
0.56345	0.30449	0.39189	0.17156	0.9066	129.71	−109.47
0.47243	0.30170	0.32990	0.14253	0.7575	126.07	−111.41
0.37803	0.30137	0.26410	0.11393	0.6059	122.85	−113.16
0.28481	0.30578	0.19772	0.08709	0.4590	120.56	−118.49
0.17805	0.32404	0.12035	0.05770	0.2934	119.98	−128.53
0.10347	0.36066	0.06615	0.03732	0.1781	122.22	−144.2
			25°C			
1.01265	0.22654	0.78325	0.22940	1.4715	140.49	−71.4
0.79727	0.21837	0.62317	0.17410	1.1455	131.82	−66.8
0.56345	0.21169	0.44417	0.11928	0.8020	123.85	−63.1
0.47243	0.21074	0.37287	0.09956	0.6716	121.54	−62.2
0.37803	0.21186	0.29794	0.08009	0.5382	120.04	−61.8
0.28481	0.21689	0.22304	0.06177	0.40835	120.08	−62.4
0.17805	0.23388	0.13641	0.04164	0.2613	123.98	−65.9
0.10347	0.26673	0.07587	0.02760	0.1587	132.63	−74.0
			40°C			
1.01265	0.1487	0.86207	0.15058	1.3138	111.05	−38.3
0.79727	0.14403	0.68244	0.11483	1.0269	106.09	−35.76
0.56345	0.14053	0.48427	0.07918	0.7218	101.97	−33.92
0.47243	0.14037	0.40611	0.06632	0.6051	101.21	−33.02
0.37803	0.14176	0.32444	0.05359	0.4852	101.45	−32.63
0.28481	0.14609	0.24320	0.04161	0.3680	103.52	−32.77
0.17805	0.15967	0.14962	0.02843	0.2349	110.84	−35.36
0.10347	0.18589	0.08424	0.01923	0.1419	124.45	−40.88

Table 4.4: (continued)

m_2 (mol kg^{-1})	α	$(1-\alpha)m_2$ (mol kg^{-1})	αm_2 (mol kg^{-1})	I (mol kg^{-1})	${}^{\phi}C_p^{rel}$ (J K^{-1}mol^{-1})	${}^{\phi}C_p^{exp} - {}^{\phi}C_p^{rel}$ (J K^{-1}mol^{-1})
			55°C			
1.01265	0.095565	0.91588	0.09677	1.2062	80.44	−15.26
0.79727	0.092715	0.72335	0.07392	0.9451	78.00	−14.63
0.56345	0.090670	0.51236	0.05109	0.6656	76.43	−14.67
0.47243	0.090686	0.42959	0.04284	0.5581	76.59	−15.01
0.37803	0.091761	0.34334	0.034688	0.4474	77.70	−15.38
0.28481	0.094856	0.25779	0.02702	0.3388	80.56	−15.95
0.17805	0.10447	0.15945	0.01860	0.2153	88.80	−17.97
0.10347	0.12332	0.09071	0.01276	0.1290	103.75	−20.03

properties. However, these fits are useful for interpolation purposes and are listed in Table 4.5 along with the data cited above. Representative plots of the apparent molar volumes and heat capacities for the desired species $H[HSO_4]$ minus the extended form of the Debye-Hückel equation, are shown in Figures 4.5 and 4.6.

4.4 Standard state properties

4.4.1 Direct comparisons

Many of the room temperature standard state partial molar volumes and heat capacities for nitric and perchloric acids were discussed in Chapter 2 and the preferred values at 25° are still valid. For temperatures above and below 25°C there are results from only a few studies that can be compared with the present work. MILLERO (1972) cites standard state volumes from ZEN (1957) at 0, 10, and 25°C, of which the 10 and 25° data are in good agreement with the present results. SMITH-MAGOWAN and GOLDBERG (1979) cite several investigations of the heat capacities of aqueous nitric acid solutions. None of the results that were derived from temperature dependent studies are of sufficient precision or to low enough ionic strengths for useful comparisons. It is expected that the present results are the most useful over this reported temperature range.

There are more recent data that lead to standard state volumes and heat capacities for perchloric acid. The recent precise volumetric results of HERRINGTON *et al.* (1985) from 25 to 75°C are in excellent agreement with the present results. SMITH-MAGOWAN and GOLDBERG (1979) have compiled a listing of all heat capacity measurements on perchloric acid prior to 1979 from which it can be seen that no study covers this broad of a temperature range. The only direct results obtained as a function of temperature were made in 1892. Again it is felt that the present results are the most reliable over the temperature range 10 to 55°C.

MILLERO (1972) cites values for the standard state volume of sulphuric acid in its completely dissociated state ($2H^+ + SO_4^{2-}$). Precise volumetric results are available from LINDSTROM and WIRTH (1969), who have also calculated the equilibrium constants as a function of ionic strength by application of Young's rule. Their results have also led to $\bar{V}°(H^+ + HSO_4^-, aq) = 35.68$ cm^{3}mol^{-1}. Dilatometric titrations by

Table 4.5: Standard state partial molar volumes, heat capacities, and ionic strength parameters for aqueous (H^+, HSO_4^-) from 10 to 55°C.*

t (°C)	${}^{\phi}V_2^{\circ}$ (cm^3mol^{-1})	B_V ($cm^3kg\ mol^{-2}$)	C_V ($cm^3kg^{3/2}mol^{-5/2}$)
10	34.52 ± 0.39	8.174 ± 1.52	-3.280 ± 1.07
25	36.82 ± 0.14	4.522 ± 0.65	-1.839 ± 0.49
40	38.22 ± 0.11	3.973 ± 0.55	-1.997 ± 0.44
55	39.06 ± 0.13	1.091 ± 0.68	-0.277 ± 0.56

t (°C)	${}^{\phi}C_{p,2}^{\circ}$ ($JK^{-1}mol^{-1}$)	B_C ($J\ kg\ K^{-1}mol^{-2}$)	C_C ($J\ kg^{3/2}K^{-1}mol^{-5/2}$)
10	-47.2 ± 1.0	-19.40 ± 4.0	-20.43 ± 2.85
25	-17.8 ± 0.8	-48.25 ± 3.0	15.29 ± 2.2
40	-9.2 ± 0.5	-49.86 ± 2.3	21.07 ± 1.8
55	-4.4 ± 1.5	-56.33 ± 8.1	32.69 ± 6.8

* For (H^+, HSO_4^-) interpolations between experimental temperatures from 10 to 55°C use:

$B_V = 78.790 - 0.35046T + 0.00034913T^2$

$C_V = 36.175 - 0.30376T + 0.00058540T^2$

$B_C = 2594.81 - 16.631T + 0.026102T^2$

$C_C = -3025.83 + 18.913T - 0.029283T^2$

$T/K = t/°C + 273.15$

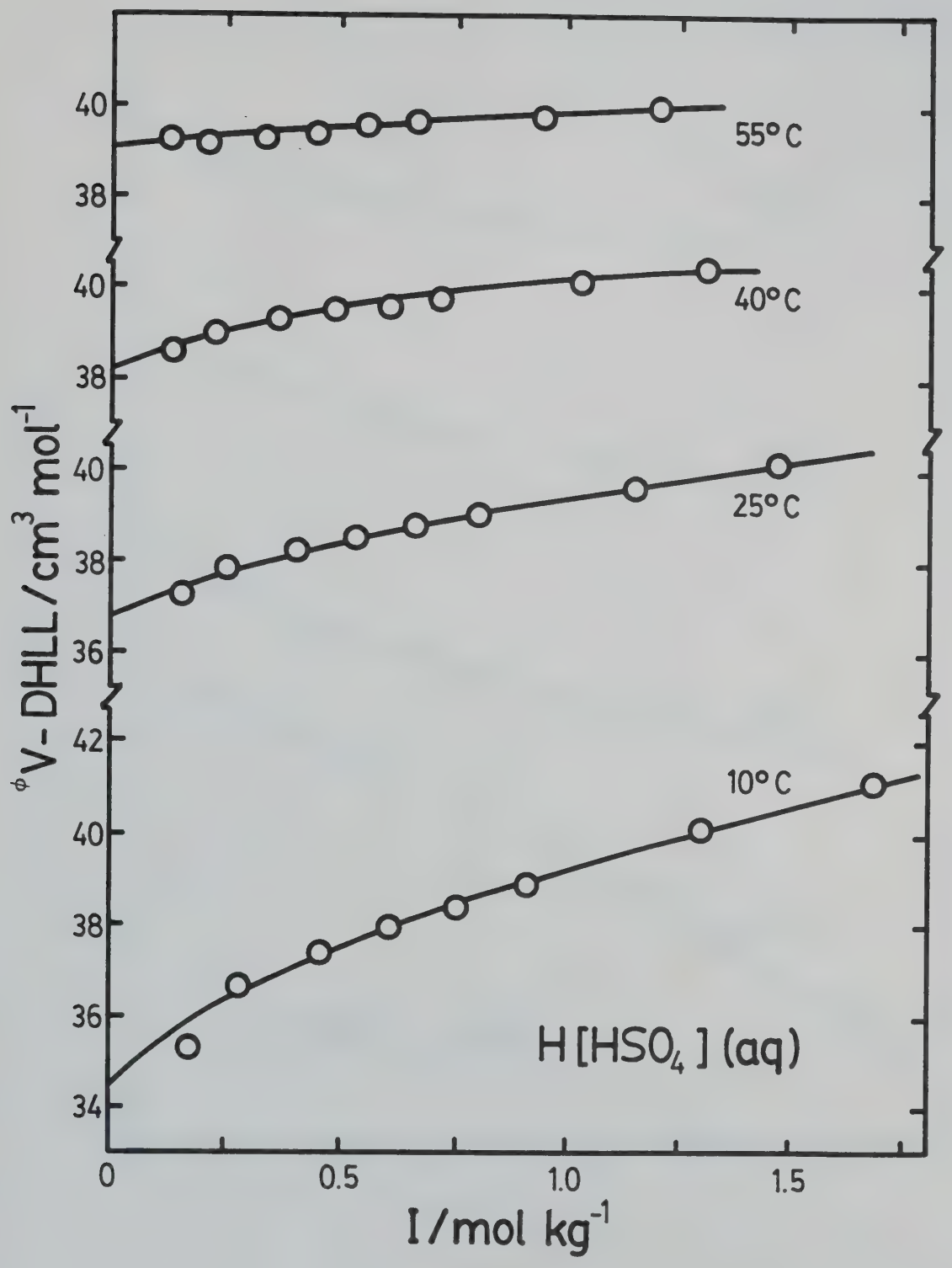

Figure 4.5: $^{\phi}V$ minus the extended Debye-Hückel limiting law (DHLL) for aqueous (H^+, HSO_4^-) from 10 to 55°C versus ionic strength. Lines are least squares fits of eq. 4.20

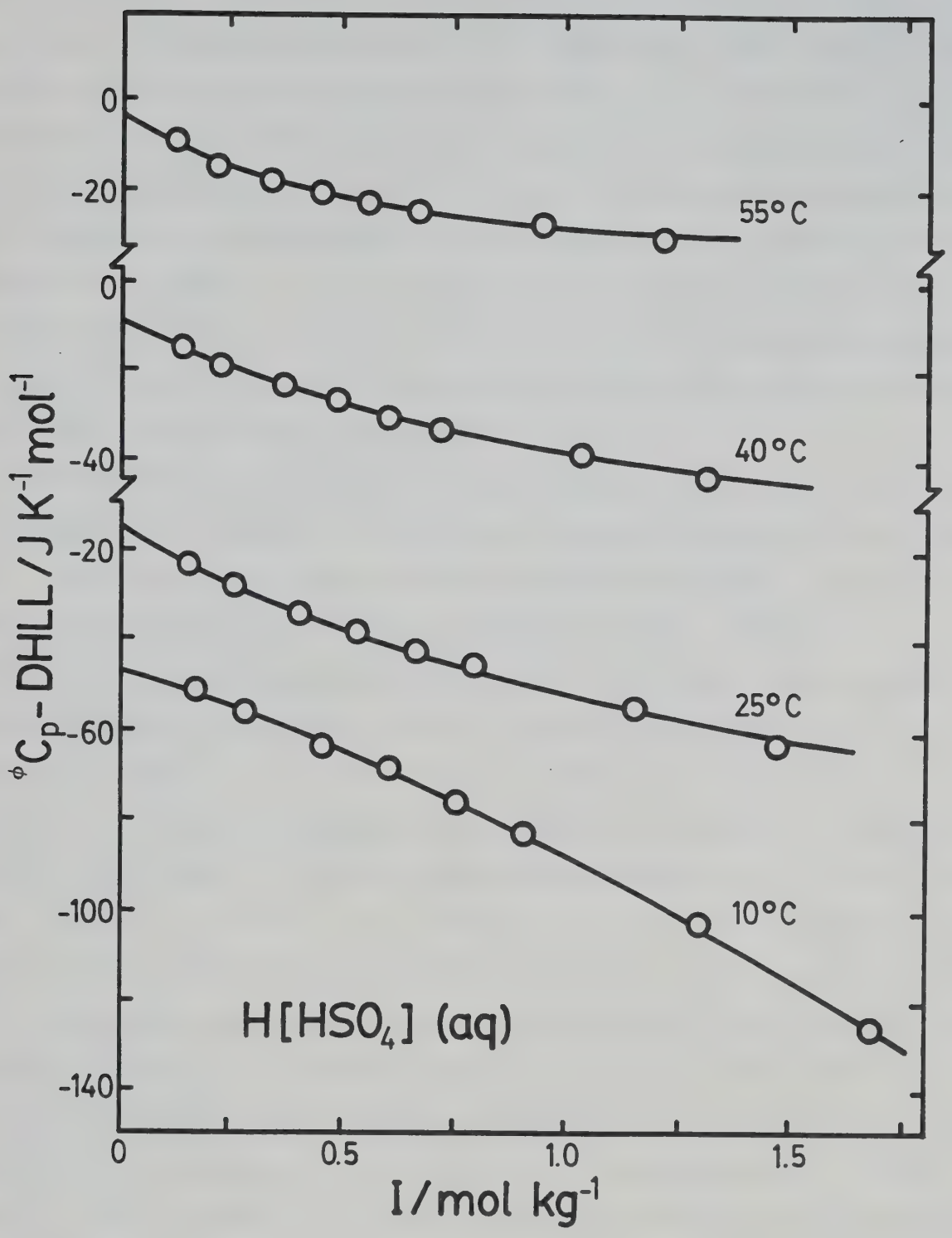

Figure 4.6: ${}^{\phi}C_p$ minus the extended Debye-Hückel limiting law (DHLL) for aqueous (H^+, HSO_4^-) from 10 to 55°C versus ionic strength. Lines are least squares fits of eq. 4.20

ROHWER *et al.* (1975) have led to ΔV° -20.0 ± 1.0 cm^3mol^{-1} for the dissociation of bisulphate ion. Combination of this value with the selected $\bar{V}^\circ(SO_4^{2-}, aq)$ = 14.2 cm^3mol^{-1} (Chapter 2), leads to $\bar{V}^\circ(H^+ + HSO_4^-, aq)$ = 34.2 ± 1.0 cm^3mol^{-1}. LARSON *et al.* (1982) have reported $\bar{V}^\circ(H^+ + HSO_4^-, aq)$ = 35.2 cm^3mol^{-1} based on their volumetric data combined with their choice of equilibrium constant and activity coefficients. Recalculations using their raw data with the present scheme leads to $\bar{V}^\circ(H^+ + HSO_4^-, aq)$ = 36.3 ± 0.25 cm^3mol^{-1}. It can be seen that the early results of LARSON *et al.* (1982) are in good agreement with the present $\bar{V}^\circ(H^+ + HSO_4^-, aq)$ = 36.82 ± 0.14 cm^3mol^{-1} while the recalculated result is in even better agreement. A weighted average of all of the results discussed above leads to the selected value $\bar{V}^\circ(H^+ + HSO_4^-, aq)$ = 36.7 ± 0.3 cm^3mol^{-1}.

For standard state partial molar heat capacities, there are several studies at room temperature and at elevated temperatures (SMITH-MAGOWAN and GOLDBERG, 1979). The best results at room temperature are those of LARSON *et al.* (1982), who considered relaxational contributions to the heat capacities. Because of the narrow ionic strength range investigated by these authors, they did not observe some of the problems discussed earlier in this Chapter. The present relaxation contributions are significantly larger than those reported by LARSON *et al.* (1982). Recalculation of their results with the presently reported scheme led to $\bar{C}_p^\circ(H^+ + HSO_4^-, aq)$ = -27.2 ± 1.5 J $K^{-1}mol^{-1}$. This is in fairly good agreement with the present result $\bar{C}_p^\circ(H^+ + HSO_4^-, aq)$ = -16.5 ± 0.7 J $K^{-1}mol^{-1}$, considering the difficulty in data analysis. Here it should be emphasized that the ± values listed refer to the "goodness of fit" and provide only a lower limit to the uncertainty in the reported result. Because of the wider ionic strength dependence, the present value is preferred.

Results of integral heat of solution measurements (READNOUR and COBBLE, 1969) have led to definition of the standard state heat capacity of $(H^+ + HSO_4^-, aq)$ from 0 to 100°C. LARSON *et al.* (1982) have noted from a personal communication with C.M. Criss that the reported ΔC_p° value for the dissociation of bisulphate to sulphate ion of -356 J $K^{-1}mol^{-1}$ has been revised by Criss to -280 J $K^{-1}mol^{-1}$. Using this ΔC_p°, and the selected standard state heat capacity value for sulphate ion of -282 J $K^{-1}mol^{-1}$ (Chapter 2), leads to $\bar{C}_p^\circ(H^+ + HSO_4^-, aq)$ = -2 J $K^{-1}mol^{-1}$ which is in reasonable agreement with the direct calorimetric results from the present study and

from LARSON *et al.* (1982).

It should be noted here that because of uncertainties associated with chemical relaxation and speciation calculations, the integral heat of solution measurements made by Cobble and coworkers may be particularly suited to these types of heat capacity determinations. It is likely that the errors associated with differentiation of enthalpy results to obtain heat capacities may be marginally smaller (or perhaps a little larger) than uncertainties associated with the present approach, as discussed earlier in this Chapter.

Several values of ΔC_p° can also be calculated for the bisulphate dissociation reaction from equilibrium constant results obtained over a range of temperatures. These values are considered to have much larger uncertainties than the "thermal values" discussed previously because of the large errors associated with double differentiation of equilibrium constants.

4.4.2 Temperature dependence of standard state properties

It is useful to have analytical represention of the temperature dependence of the standard state partial molar volumes and heat capacities for all of the solutes under present investigation for use in various thermodynamic calculations. One of the most useful representations of the temperature dependence of standard state properties is the equation suggested by HOLMES and MESMER (1983):

$$\bar{Y}^\circ = a + \frac{b}{T-\theta} + cT + dT^2 \tag{4.61}$$

For ease of calculations involving many species, and from fits of the standard state heat capacities of HCl(aq) from 10 to 140°C (TREMAINE *et al.*, 1986), the temperature represented by θ has been assigned the value 190 K. Most of the fits presented below have been made with data resulting solely from the present work. The fit to standard state volumes of perchloric acid included the accurate results of WIRTH and COLLIER (1950), and all of the results from HERRINGTON *et al.* (1985) except their 75° point. Fitting of equations of type (4.61) (using only 3 of the 4 parameters available) to the selected standard state properties has led to:

$$\bar{V}^\circ(\mathrm{HClO_4},\ \mathrm{aq}) \ = \ -107.79 + 0.87322T - 0.0012203T^2 \tag{4.62}$$

$$\bar{C}_p^\circ(\mathrm{HClO_4,\ aq}) = 1408.1 - \frac{55801}{T-190} - 3.0767T \quad (4.63)$$

$$\bar{V}^\circ(\mathrm{HNO_3,\ aq}) = 76.67 - \frac{2210.1}{T-190} - 0.090063T \quad (4.64)$$

$$\bar{C}_p^\circ(\mathrm{HNO_3,\ aq}) = 1154.9 - \frac{49213}{T-190} - 2.5850T \quad (4.65)$$

$$\bar{V}^\circ(\mathrm{H[HSO_4],\ aq}) = 84.05 - \frac{2384.3}{T-190} - 0.084510T \quad (4.66)$$

$$\bar{C}_p^\circ(\mathrm{H[HSO_4],\ aq}) = 1040.4 - \frac{41198}{T-190} - 2.2773T \quad (4.67)$$

All of these equations are valid over the temperature range from 10 to 55°C, except the expression for $\bar{V}^\circ(\mathrm{HClO_4,\ aq})$, that is valid from 10 to 65°C. Plots of the standard state partial molar volumes and heat capacities are shown for all three solutes in Figures 4.7 to 4.12. The "goodness of fit" of the above expressions, and the marked temperature dependence of these properties can be seen. These expressions should be used for all calculations requiring the standard state volumes and heat capacities over these specified temperature ranges, rather than the expressions that are derived in the next section for use over wider ranges of temperature.

Conventional ionic volumes and heat capacities of the ions $\mathrm{NO_3^-(aq)}$, $\mathrm{ClO_4^-(aq)}$, and $\mathrm{HSO_4^-(aq)}$ can be derived from the convention $\bar{Y}^\circ(\mathrm{H^+,\ aq}) \equiv 0$ at all temperatures. Since all of the species that are under present investigation are acidic species, these conventional ionic properties are exactly equivalent to the standard state properties.

4.5 Discussion

4.5.1 Helgeson–Kirkham–Flowers model

As mentioned in the discussion, the change in standard state heat capacity of a chemical reaction is related to the second derivative of the equilibrium constant with respect to temperature. Equilibrium constants or Gibbs free energies can be calculated at elevated temperatures using heat capacity data providing that room temperature equilibrium and enthalpy data are available. Because the relationship between equilibrium constants (or Gibbs free energies) and heat capacities is through the second derivative with respect to temperature (see eqs. 4.1-4.3), shortcomings in

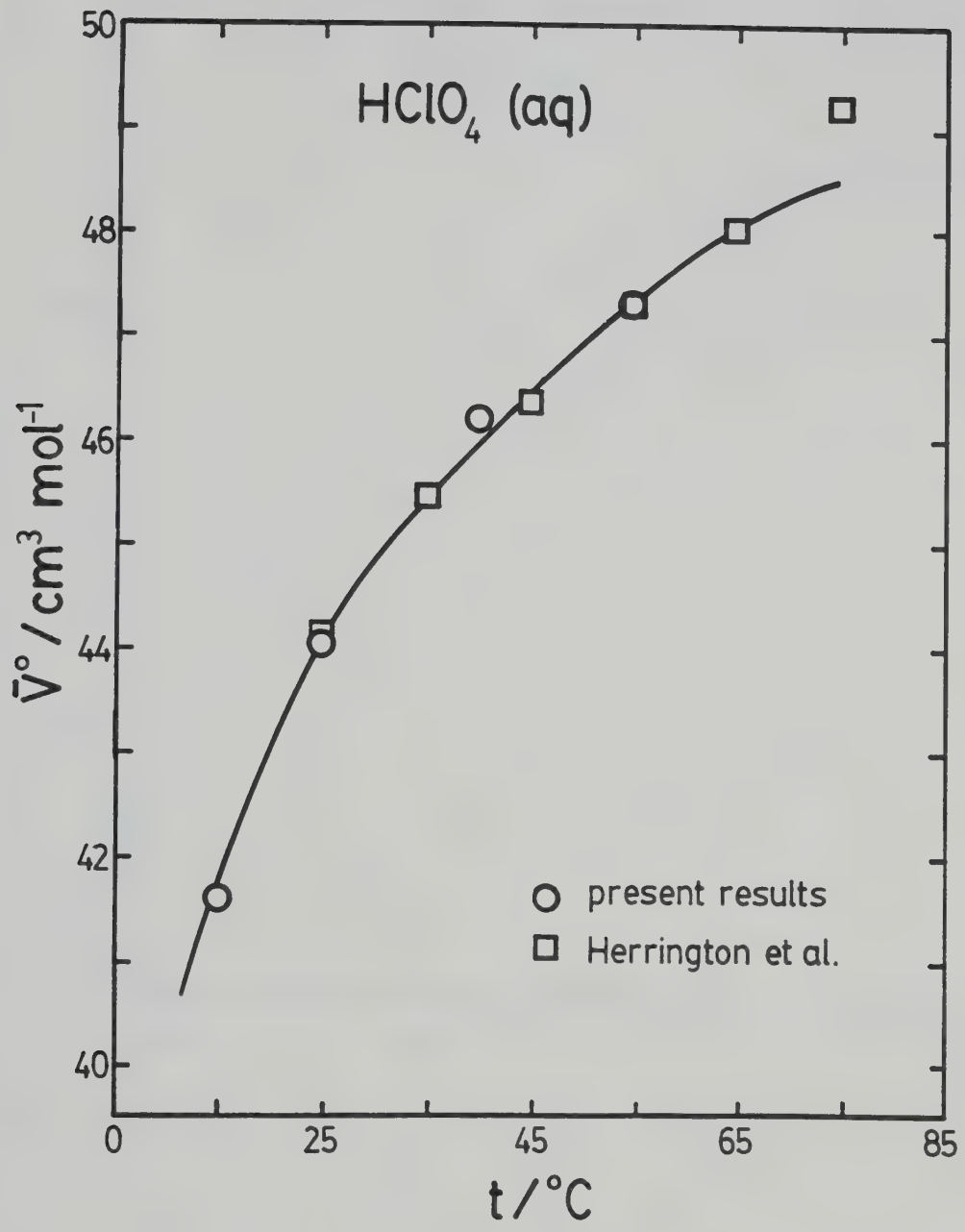

Figure 4.7: Standard state volumes for $HClO_4$ from 10 to 65°C.

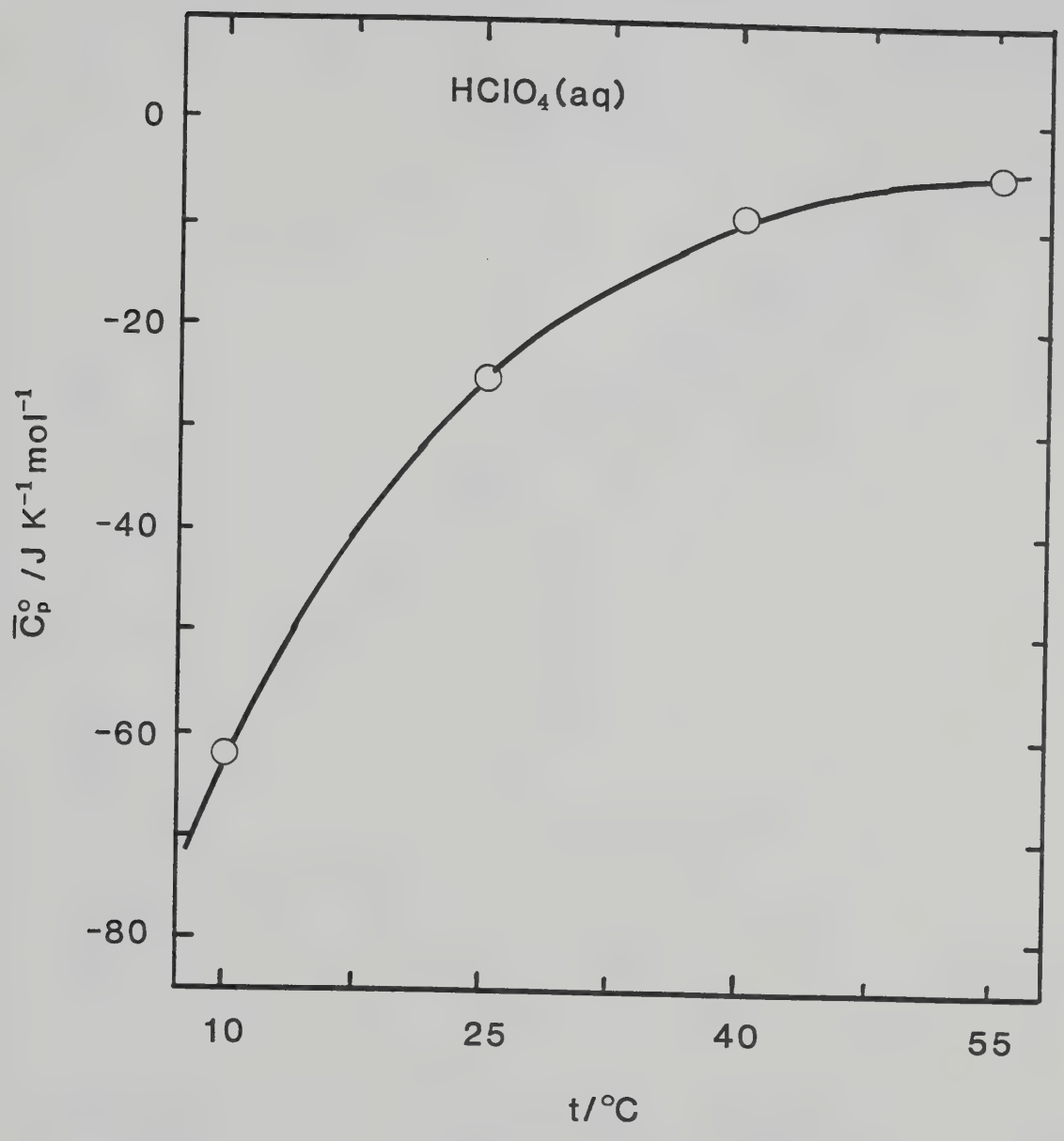

Figure 4.8: Standard state heat capacities for $HClO_4$ from 10 to 55°C.

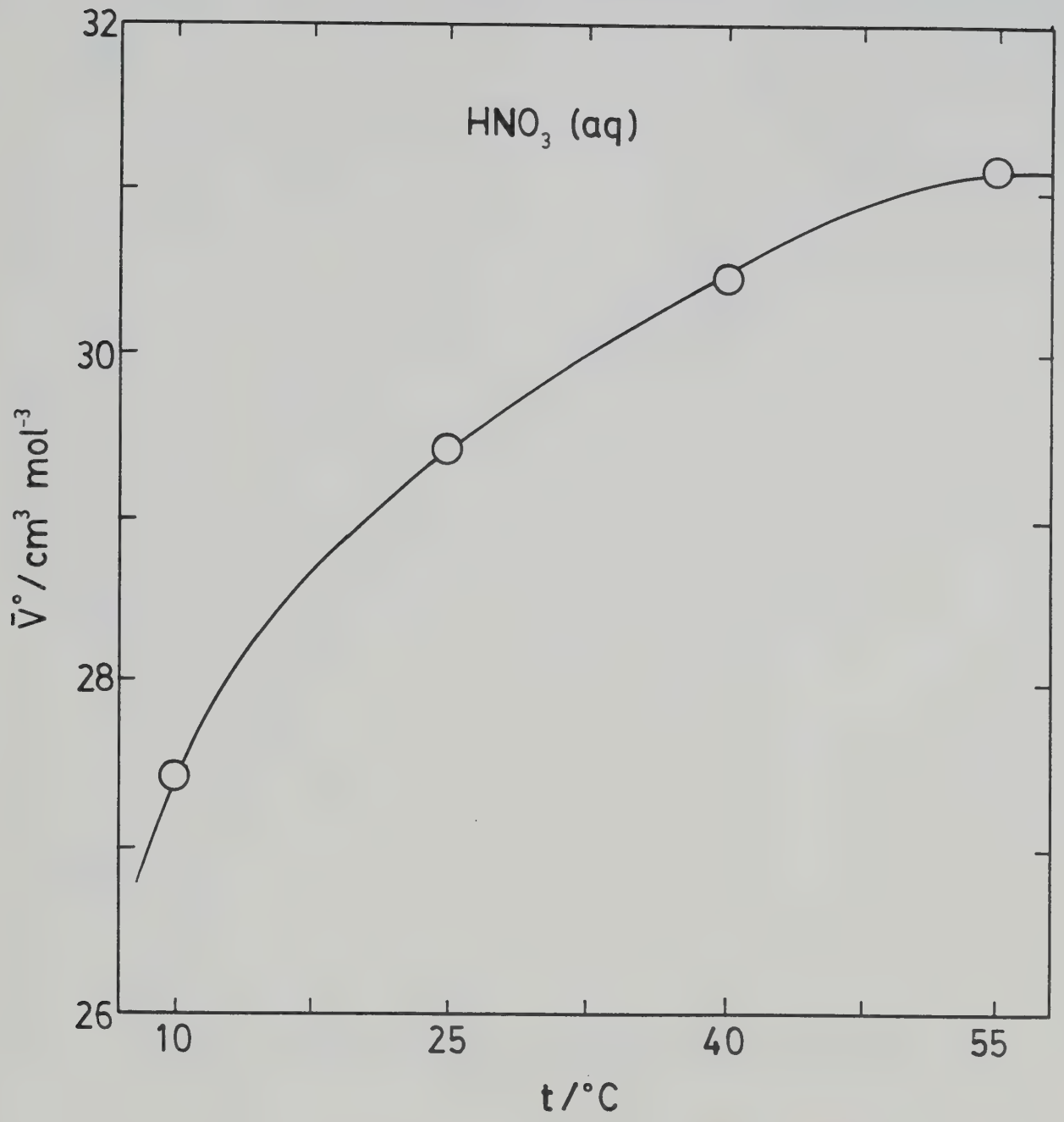

Figure 4.9: Standard state volumes for HNO_3 from 10 to 55°C.

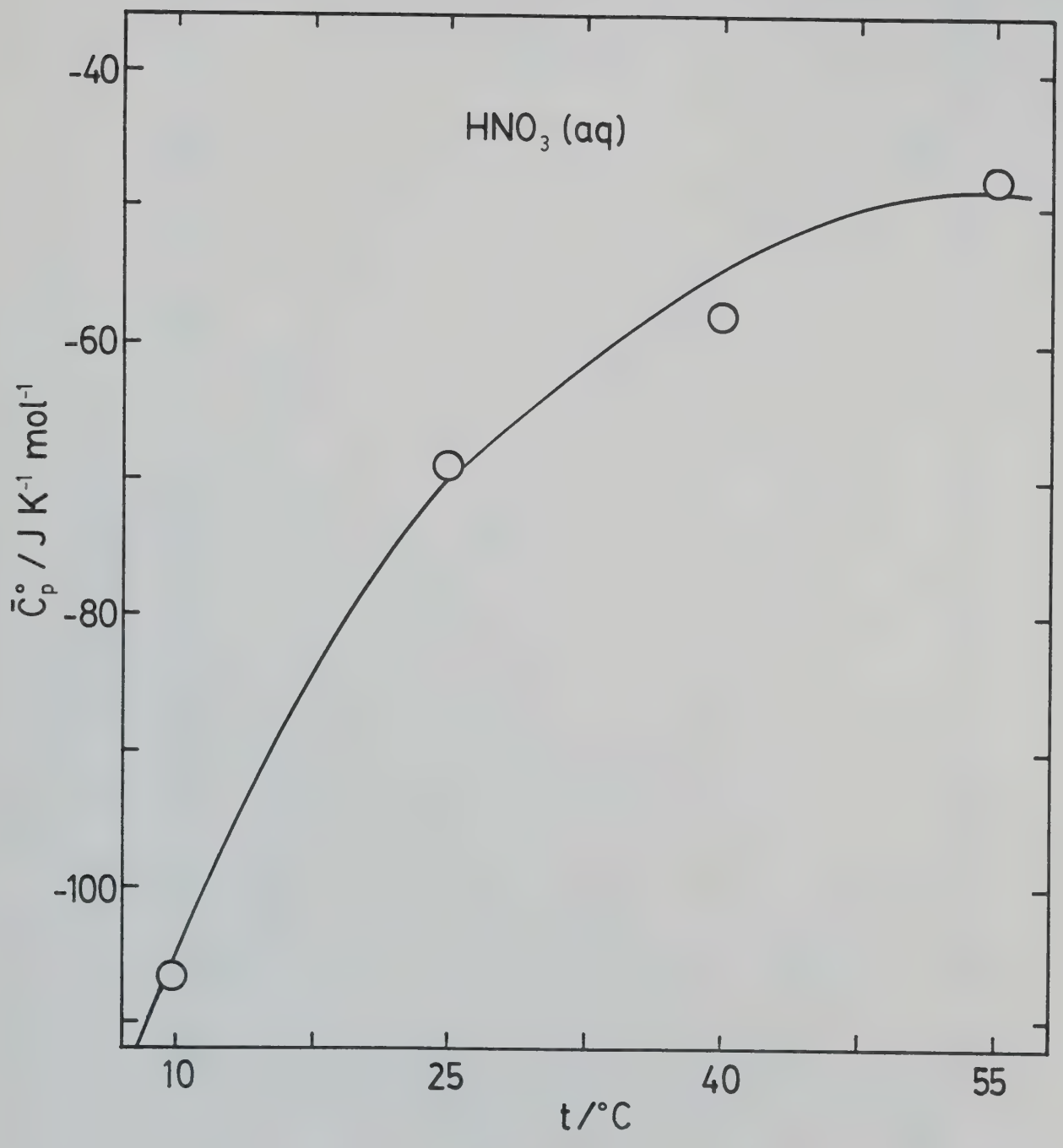

Figure 4.10: Standard state heat capacities for HNO_3 from 10 to 55°C.

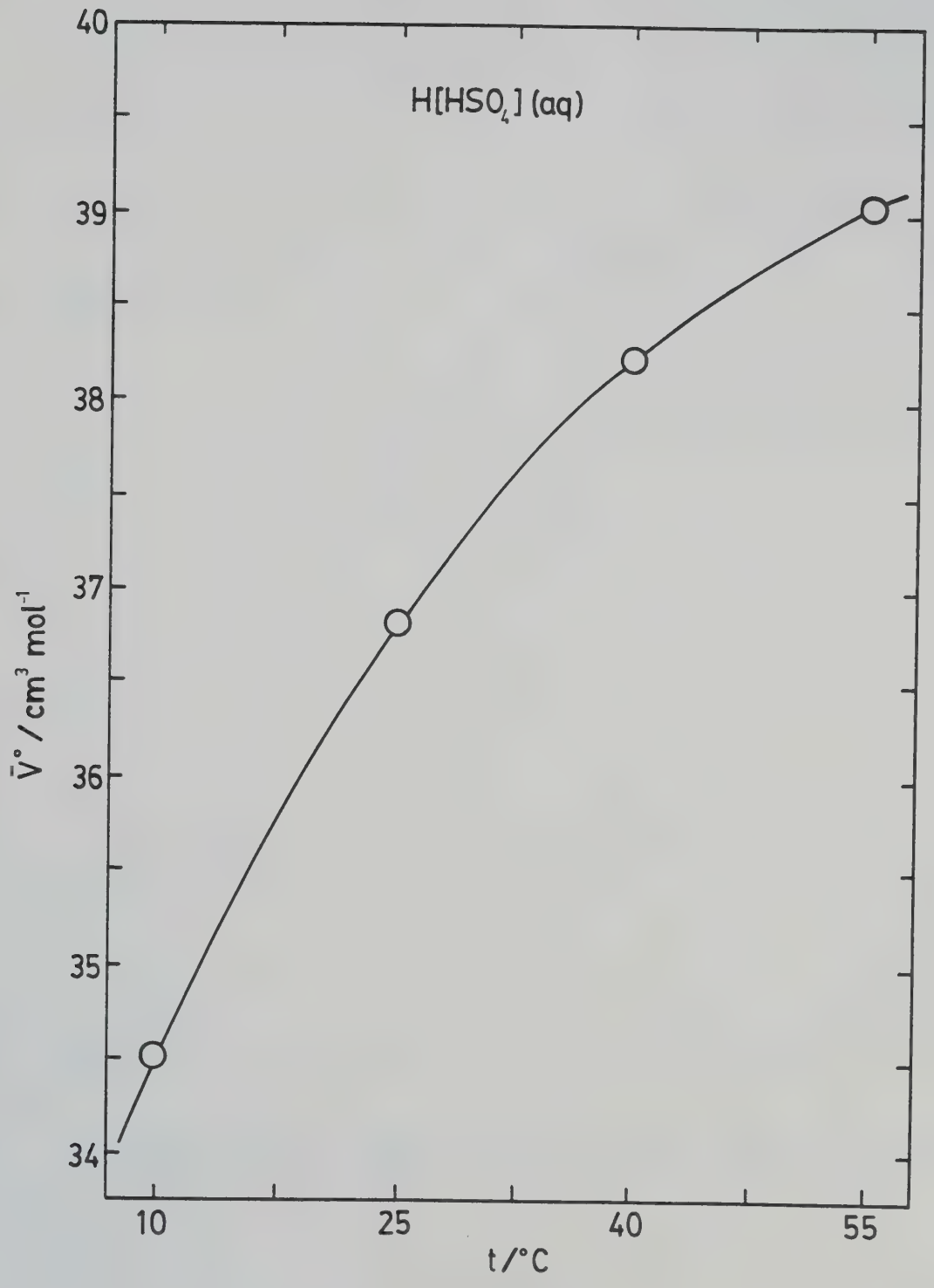

Figure 4.11: Standard state volumes for (H^+, HSO_4^-) from 10 to 55°C.

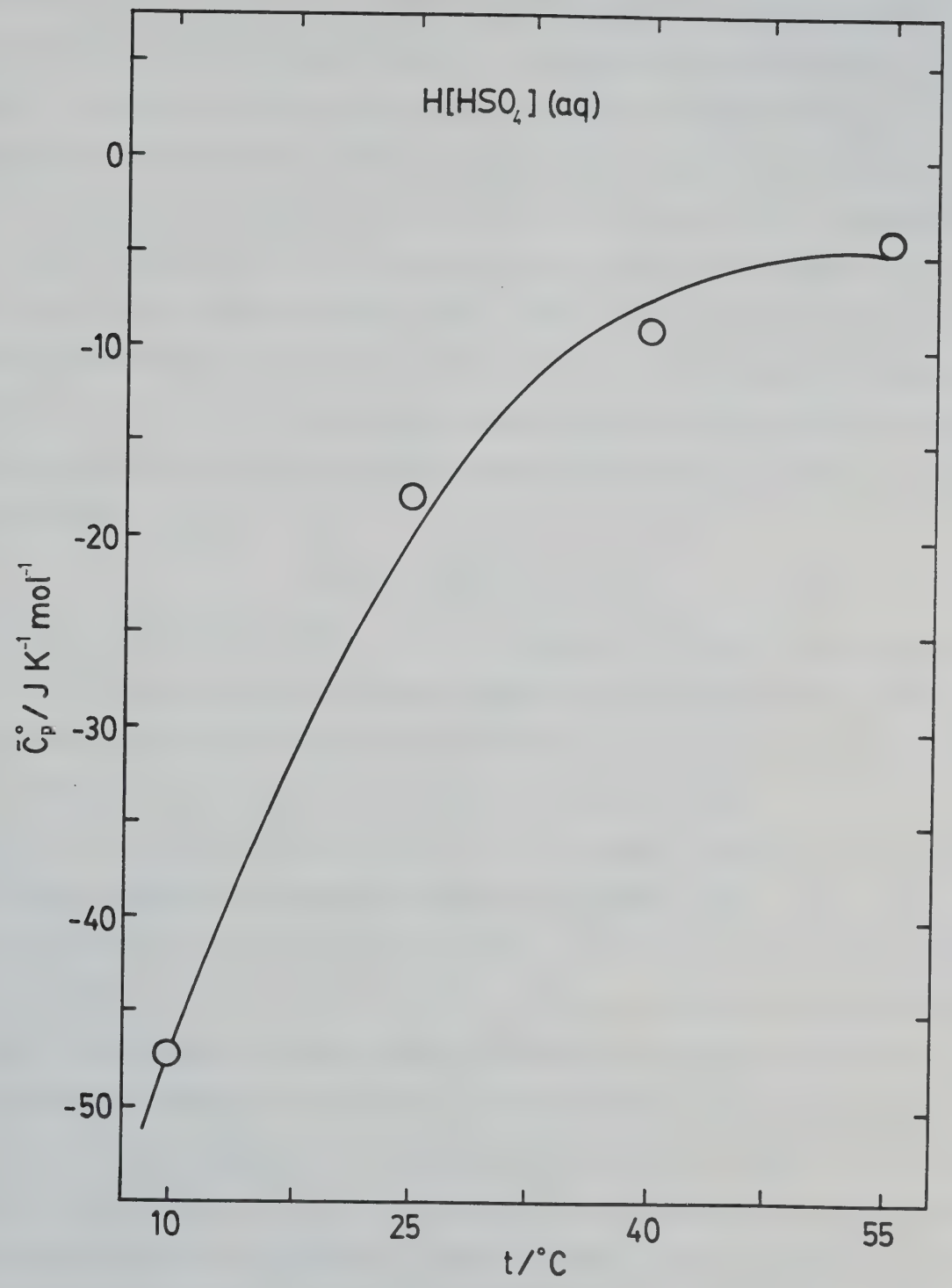

Figure 4.12: Standard state heat capacities for (H^+, HSO_4^-) from 10 to 55°C.

heat capacity functions normally have only a small effect on calculations of Gibbs free energies. Accordingly, the calculation of heat capacities from equilibrium constants can only be reliably done if there are no shortcomings in these data. The heat capacity change of a reaction is thus better suited to predictive schemes for shortcomings here have little effect whereas shortcomings in predicitive schemes for the properties themselves (equilibrium constants) would have a more dramatic effect.

A classic description of the thermodynamic properties of aqueous ions is provided by the Born equation (BORN, 1920). The Born equation can be derived by considering the difference in free energy of charging a hard sphere (of fixed radius) in *vacuo* and in a solvent that can be regarded as a continuous dielectric medium from the surface of the ion to an infinite distance from the ion. The Born equation is shown below

$$\Delta G = \frac{N_A z^2 e^2}{8\pi\epsilon_o r}\left(\frac{1}{\epsilon} - 1\right) \tag{4.69}$$

where N_A is Avagadro's number, z is the charge of the ion, e is the charge of an elctron, ϵ_o is the permitivitty of vacuum, and r is the radius of the ion. The radius most consistent with the derivation of the Born equation is the size of the solvent cavity that is occupied by the ion (RASHIN and HONIG, 1985).

There are numerous difficulties with use of the Born equation for solutions near room temperature [see for example RASHIN and HONIG (1985)]. Most of the problems are related to the inadequate assumption that water is a continuous dielectric fluid (especially near an ion where dielectric saturation is known to occur) and to uncertainties in assigning ionic radii to solutes in water. Generally these radii are larger and are denoted "effective" aqueous radii. The dielectric constant of water decreases from a value of approximately 78 at 25°C to less than 20 at 300°C (UEMATSU and FRANCK, 1980). It is expected that because of this decrease in the static dielectric constant (due mainly to breakdown of ordered water structure because of increased thermal motion) the Born equation will become better at representing thermodynamic properties as the temperature is increased. HELGESON *et al.* (1974a,b, 1976, 1981) have applied the Born equation with these shortcomings in mind.

The Born equation can be represented by (HELGESON *et al.*, 1981)

$$\Delta G = \omega\left(\frac{1}{\epsilon} - 1\right) \tag{4.70}$$

where $$\omega = 6.94657 \times 10^5 \left(\frac{z^2}{r}\right) \text{ Å J mol}^{-1} \tag{4.71}$$

The conventions expressed earlier regarding partial molar properties for ions based on conventions for $H^+(aq)$ (conventional and absolute ionic properties), also apply here for ω values for *ions* (for calculation of the standard as opposed to the conventional partial molar Gibbs free energy of solvation). The relationship of these different ω values for ions is shown below:

$$\omega^{abs} = \omega_{conv} + z\omega^{abs}_{H^+} \tag{4.72}$$

where ω^{abs} is the "absolute" property of the ion, ω_{conv} is the conventional property based on $\omega^{abs}_{H^+} \equiv 0$, z is the charge of the ion, and $\omega^{abs}_{H^+}$ is equal to the "absolute" ω for the aqueous hydrogen ion. No such complications are present when considering solutes as the sum of their ionic components.

The Helgeson–Kirkham–Flowers equations of state for standard state volumes and heat capacities have the form (HELGESON *et al.*, 1981)

$$\bar{V}^\circ = a_1 + a_2 p + \frac{a_3 T + a_4 pT}{T - \theta} + \Delta V_{BORN} \tag{4.73}$$

$$\bar{C}^\circ_p = c_1 + \frac{c_2 T}{T - \theta} - \frac{\theta T \left[2a_3(p-1) + a_4(p^2 - 1)\right]}{(T-\theta)^3} + \Delta C_{p,BORN} \tag{4.74}$$

where all a, c, and θ terms are fitting coefficients. The ΔY_{Born} terms come directly from the relationship of the partial molar free energy to partial molar volumes and heat capacities

$$\Delta V_{Born} = \left(\frac{\partial \Delta G_{Born}}{\partial p}\right)_T \tag{4.75}$$

$$= \omega \left(\frac{\partial \frac{1}{\epsilon}}{\partial p}\right)_T \tag{4.76}$$

$$= -\omega \frac{1}{\epsilon} \left(\frac{\partial \ln \epsilon}{\partial p}\right)_T \tag{4.77}$$

$$= -\omega Q \tag{4.78}$$

$$\Delta C_{p,Born} = -T \left(\frac{\partial^2 \Delta G_{Born}}{\partial T^2}\right)_p \tag{4.79}$$

$$= -\omega T \left(\frac{\partial^2 \frac{1}{\epsilon}}{\partial T^2}\right)_p \tag{4.80}$$

$$= \omega T \frac{1}{\epsilon}\left[\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_p - \left(\frac{\partial \ln \epsilon}{\partial T}\right)_p^2\right] \quad (4.81)$$

$$= \omega T X \quad (4.82)$$

where Q and X are shorthand notations for various pressure and temperature dependences of the dielectric constant that result from the Born equation. Numerical values for these terms were taken from HELGESON and KIRKHAM (1974, 1976).

Since the present results were obtained at constant pressure, eqs. 4.73 and 4.74 reduce to:

$$\bar{V}^\circ = \sigma + \frac{\xi T}{T - \theta} + \Delta V_{BORN} \quad (4.83)$$

$$\bar{C}_p^\circ = c_1 + \frac{c_2 T}{T - \theta} + \Delta C_{p,BORN} \quad (4.84)$$

The first two terms in each equation above are purely empirical and are most important at low temperatures where the Born model is least satisfactory. The third term in each equation results entirely from the Born equation that dominates at high temperatures where the model is most satisfactory. Because of the balance of empirical and theoretical components, the HKF treatment is particularly well suited for extrapolation of low temperature data for standard state partial molar properties to higher temperatures. As an example, Figure 4.13 shows experimental data for HCl(aq) from TREMAINE *et al.* (1986), and ALLRED and WOOLLEY (1981). The solid curve is a fit of the HKF model to all of the data shown in the graph (from 10 to 140°C). The dashed line is a fit of *only* the 10 to 40°C data from ALLRED and WOOLLEY (1981). The agreement of the dashed curve with the full range of experimental data is excellent. This example lends confidence to application of the HKF model to the present results obtained to 55°C.

In all of these equations the "effective" radii for anionic species are equivalent to crystallographic radii, and for cationic species the effective radii are the crystallographic radii plus 0.94 Å. Effective aqueous radii for all of these solutes were calculated from the crystal "ionic radii" listed by SHANNON (1976). The results of fitting equations of the type given by eqs. 4.83 and 4.84 are listed below

$$\frac{\bar{V}^\circ(HClO_4,\ aq)}{cm^3 mol^{-1}} = 84.508 - \frac{16.465T}{T - 167.4} - 4.75415 \times 10^6 Q \quad (4.85)$$

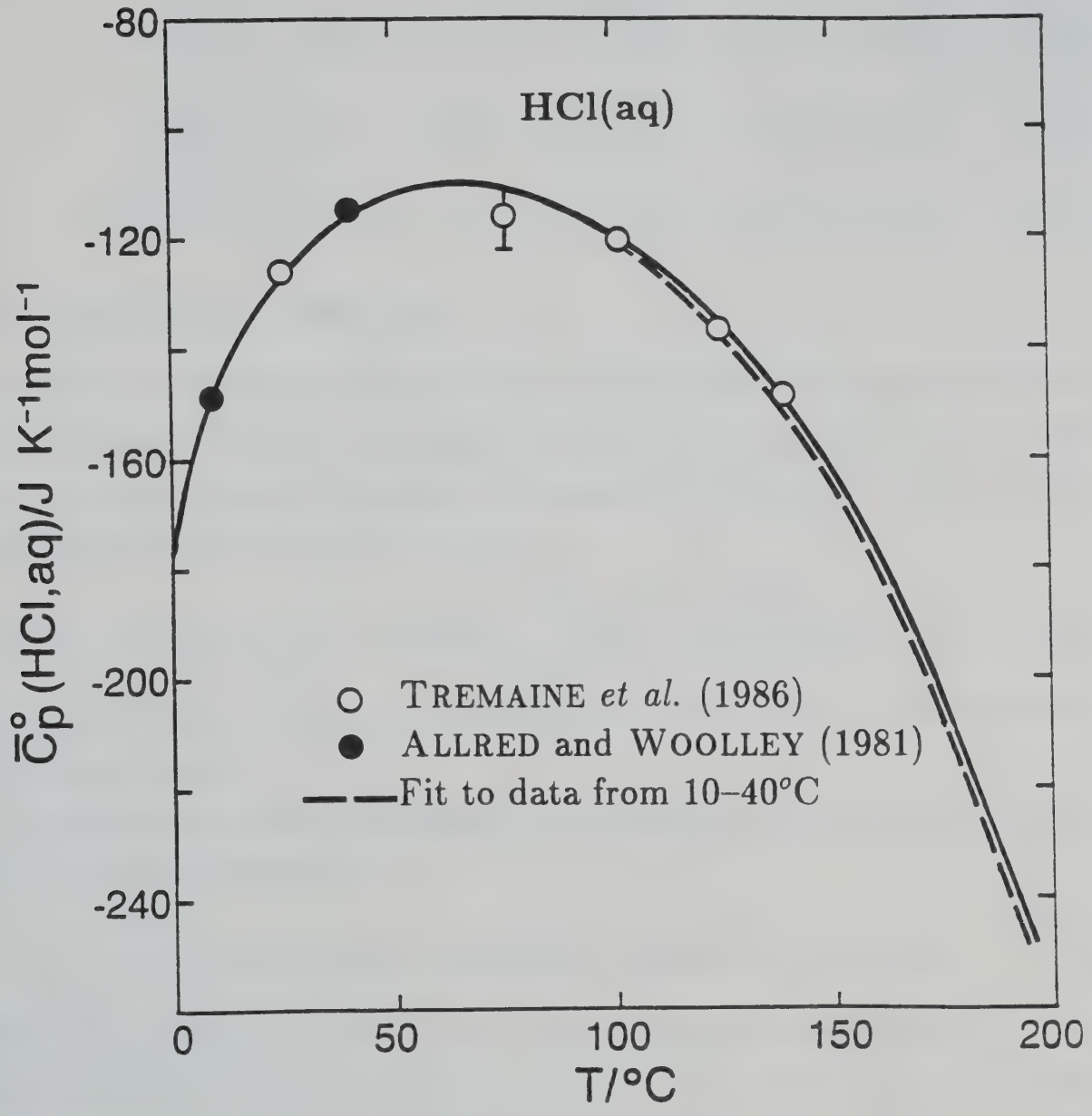

Figure 4.13: Standard state heat capacities for HCl(aq) from TREMAINE *et al.* (1986), and the results of application of the HKF model.

$$\frac{\bar{C}_p^\circ(\mathrm{HClO_4,\ aq})}{\mathrm{J\ K^{-1}mol^{-1}}} = 89.43 - \frac{8.6367T}{T-261.0} - 4.75415\times10^5 TX \quad (4.86)$$

$$\frac{\bar{V}^\circ(\mathrm{HNO_3,\ aq})}{\mathrm{cm^3mol^{-1}}} = 42.830 - \frac{2.5557T}{T-226.5} - 4.7100\times10^6 Q \quad (4.87)$$

$$\frac{\bar{C}_p^\circ(\mathrm{HNO_3,\ aq})}{\mathrm{J\ K^{-1}mol^{-1}}} = 45.36 - \frac{9.0799T}{T-259.9} - 4.7100\times10^5 TX \quad (4.88)$$

$$\frac{\bar{V}^\circ(\mathrm{H[HSO_4],\ aq})}{\mathrm{cm^3mol^{-1}}} = 53.804 - \frac{3.7327T}{T-219.8} - 4.67579\times10^6 Q \quad (4.89)$$

$$\frac{\bar{C}_p^\circ(\mathrm{H[HSO_4],\ aq})}{\mathrm{J\ K^{-1}mol^{-1}}} = 74.87 - \frac{5.7319T}{T-263.2} - 4.67579\times10^5 TX \quad (4.90)$$

4.5.2 Equilbrium calculations

As has been mentioned the second derivative of the Gibbs free energy is related to the heat capacity. The Gibbs free energy of formation of a species can be calculated over all temperatures and pressures, referenced to the elements in their standard states at 298.15 K and 1 bar according to

$$\Delta G^\circ_{f,T} = \Delta G^\circ_{f,298} - \bar{S}^\circ_{298}(T-298.15) + \int_{298}^{T}\bar{C}_p^\circ dT - T\int_{298}^{T}\frac{\bar{C}_p^\circ}{T}dT + \int_1^p \bar{V}^\circ dp \quad (4.91)$$

where $\bar{S}^\circ_{298}$ is equal to the standard state partial molar entropy of the species at 298.15 K and 1 bar.

The bisulphate-sulphate equilibrium (eq. 4.25) can be represented (in terms of species used for calculations) by

$$(\mathrm{H^+ + HSO_4^-, aq}) = \mathrm{Na_2SO_4(aq) - 2NaCl(aq) + 2HCl(aq)} \quad (4.92)$$

Gibbs free energies for the bisulphate ion were calculated using integrated versions of eqs. 4.89 and 4.90 in combination with the data listed in Table 4.6. Gibbs free energies for Na_2SO_4 were calculated from the heat capacity results of ROGERS and PITZER (1981) combined with room temperature results of DESNOYERS *et al.* (1976), and volumetric data from CONNAUGHTON *et al.* (1986). The former data are applicable from 5 to 200°C, and were shown to be consistent to 280°C by PITZER and MURDZEK (1982). The latter results were fitted by HKF expressions of the type given by eq. 4.83 for use above their range of measurement (0 to 100°C). Equilibrium data for NaCl to 300°C was taken from PITZER *et al.* (1984), and the free energies for HCl were calculated from HKF fits to the heat capacities of HCl(aq) from 10 to

Table 4.6: Selected thermodynamic values at 25°C.

Species	$\Delta G^{\circ}_{f,298}$ (kJ mol^{-1})	$\bar{S}^{\circ}_{298}$ (J K^{-1}mol^{-1})
$Na^+(aq)$	−261.905	59.0
$Cl^-(aq)$	−131.228	56.5
$SO_4^{2-}(aq)$	−744.53	20.1
$HSO_4^-(aq)$	−755.91	131.8
$H^+(aq)$	0	0

All values are from the NBS critical tables (WAGMAN *et al.*, 1982).

140°C, and volume fits from the data of HERRINGTON *et al.* (1985), and ALLRED and WOOLLEY (1981). Room temperature Gibbs free energies of formation and standard state partial molar entropies for all appropriate ions are listed in Table 4.6.

The standard state changes in the logarithm of the equilibrium constants were calculated from 0 to 275° from the data given above and the Lewis equation

$$\ln K = \frac{-\Delta G^\circ}{RT} \tag{4.93}$$

The results of these calculations are compared with the experimental measurements from 5 to 300°C in Figure 4.14. It should be pointed out that accurate Gibbs free energies are known only to 140°C for some of the required auxiliary data (heat capacity measurements for HCl are valid to 140°). As can be seen in the figure, the agreement of the present calculations with the direct results is excellent especially considering that the data of LIETZKE *et al.* (1961) are thought to be more accurate (DAWSON *et al.*, 1986). This example clearly shows the power of the HKF model in predicting high temperature equilibrium constants for reactions from heat capacity and volume data obtained over a reasonably narrow temperature interval.

High temperature extrapolations of the equilibrium constant of the bisulphate equilibrium can also be done assuming a constant heat capacity change when the reaction is written isocoulombically (same number and charge types of ions on both sides of the reaction equation):

$$HSO_4^-(aq) + OH^-(aq) = H_2O(l) + SO_4^{2-} \tag{4.94}$$

This reaction, however, isn't rigorously isocoulombic. The isocoulombic approach is most acceptable for reactions with heat capacities known only at room temperature. Examples of isocoulombic calculations for several systems are given in subsequent Chapters.

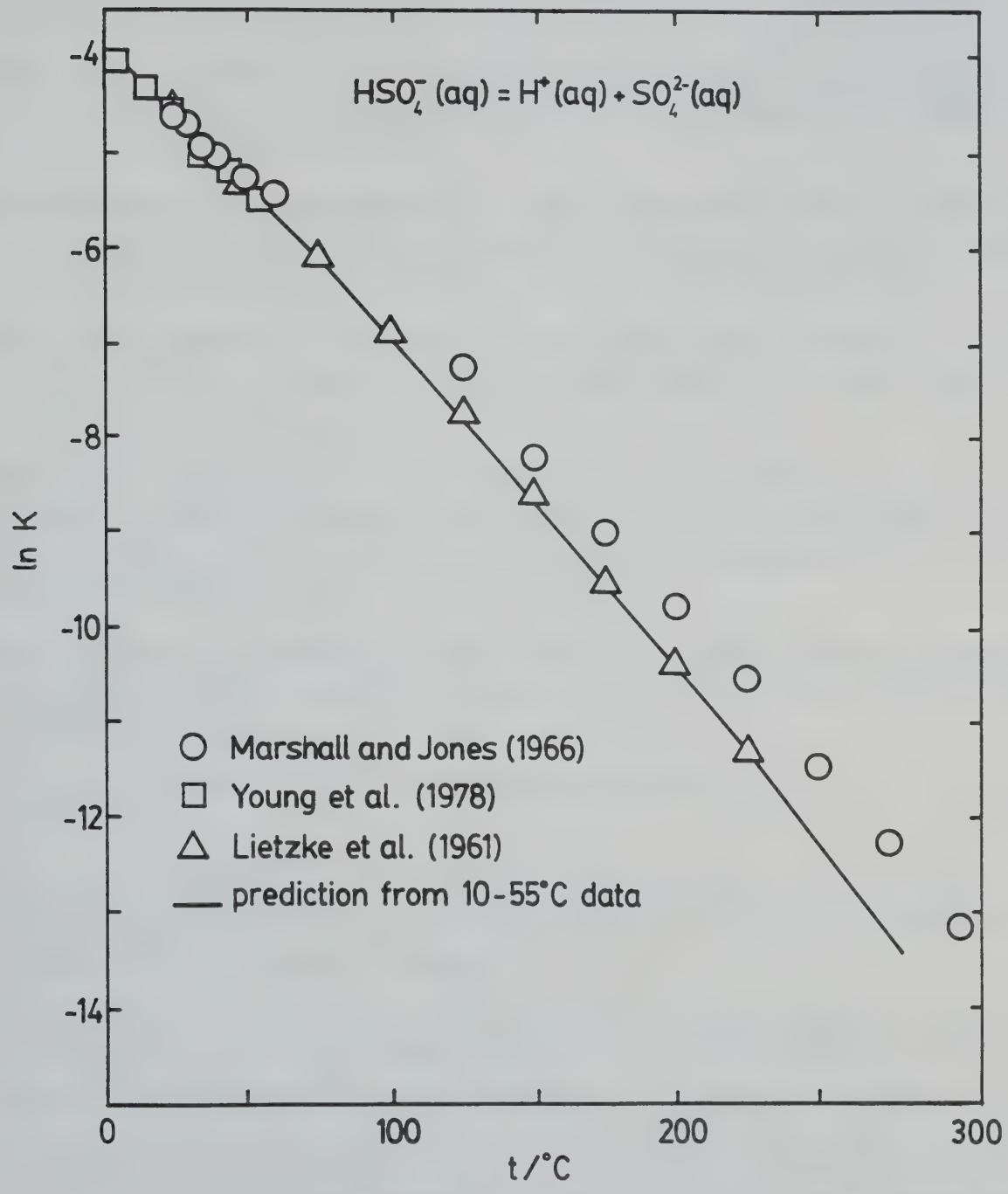

Figure 4.14: Comparison of equilibrium constants for the dissociation of bisulphate ion from direct experimental results, and predictions from the present results from 10 to 55°C as extrapolated from the HKF model.

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Chapter 5

Apparent and Partial Molar Heat Capacities and Volumes of $CrO_4^{2-}(aq)$, $HCrO_4^-(aq)$, and $Cr_2O_7^{2-}(aq)$ at 25°C : Chemical Relaxation and Calculation of Equilibrium Constants at High Temperatures.

5.1 Introduction

Thermodynamic properties of aqueous chromium(VI) species are required for a variety of applications (PALMER *et al.*, 1987), and have been the subject of numerous thermodynamic investigations and a critical review (DELLIEN *et al.*, 1976). Reliable equilibrium and enthalpy data are available for most aqueous Cr(VI) species at or near room temperature. However, there are relatively few investigations that have led to partial molar heat capacities or volumes of aqueous Cr(VI) species. It is in this context that heat capacity and density measurements have been carried out on aqueous solutions containing K_2CrO_4 and $K_2Cr_2O_7$. From results of these measurements, values for the standard state partial molar heat capacities and volumes of $CrO_4^{2-}(aq)$, $Cr_2O_7^{2-}(aq)$, and $HCrO_4^-(aq)$ have been calculated at 25°C. These quantities have then been used for several thermodynamic calculations.

Two equations that describe the equilibria between aqueous chromate and dichromate are the following:

$$CrO_4^{2-}(aq) + H_2O(l) = HCrO_4^-(aq) + OH^-(aq) \qquad (5.1)$$

$$Cr_2O_7^{2-}(aq) + H_2O(l) = 2CrO_4^{2-}(aq) + 2H^+(aq) \qquad (5.2)$$

Another important reaction is[1] is

$$Cr_2O_7^{2-}(aq) + H_2O(l) = 2HCrO_4^-(aq) \tag{5.3}$$

Although the interest in the thermodynamics of CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$ led to measurements and calculations described here before knowledge of the related research at Oak Ridge by PALMER, WESOLOWSKI, and MESMER (1987), their excellent work has provided incentives for carrying on with our investigations and refinement of the present calculation procedure. PALMER *et al.* (1987) have measured equilibrium constants for the reactions represented by eqs. 5.1-5.3 over the temperature range 25 to 175°C and have derived values for the corresponding enthalpy and heat capacity changes by applying

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \tag{5.4}$$

and

$$\left(\frac{\partial H^\circ}{\partial T}\right)_p = \Delta C_p^\circ \tag{5.5}$$

to their $K = f(T)$ results.

It is well known that the differentiation of $K = f(T)$ results required by eq. 5.4 magnifies the uncertainties and errors associated with the equilibrium measurements so that ΔH° values derived ion this way often have large uncertainites. The double differentiation that results from combined application of eqs. 5.4 and 5.5 to $K = f(T)$ results leads to further magnification of uncertainties and errors so that ΔC_p° values derived in this way often have very large uncertainties - so large as to be useless. On the other hand, the K values obtained by PALMER *et al.* (1987) are more accurate than many previously reported values, and it is especially important in this context that their measurements were made over a *much* wider range of temperatures than

[1]Examples of other equations are :

$$CrO_4^{2-}(aq) + H^+(aq) = HCrO_4^-(aq) \tag{51}a$$

$$Cr_2O_7^{2-}(aq) + 2OH^-(aq) = 2CrO_4^{2-}(aq) + H_2O(l) \tag{52}a$$

$$2HCrO_4^-(aq) = Cr_2O_7^{2-}(aq) + H_2O(l) \tag{53}a$$

Only two of all of these reactions (eqs. 5.1-5.3) are independent. Various combinations of two equations and corresponding reaction equations are enough to represent the equilibria in solutions containing CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$. Various other species including H_2CrO_4 that are present in solutions of high ionic strength are neglected here because of the conditions of the present experiments.

is common. It is therefore obvious that the ΔC_p° values derived by PALMER *et al.* are more reliable than most such values derived by way of eqs. 5.4 and 5.5, but there are still reasonable questions to be asked and perhaps answered about the relative accuracies of their values as compared with those that can be obtained from results of calorimetric measurements.

As stated above, eqs. 5.4 and 5.5 permit evaluation of ΔH° and ΔC_p° from $K = f(T)$ reults. These same equations also permit calculation of $K = f(T)$ from knowledge of K, ΔH°, and ΔC_p° at one temperature (usually $T = 298.15\ K$). Part of the original motivation for the research being described here was to carry out these calculations to obtain values for the equilibrium constants describing equilibria between $CrO_4^{2-}(aq)$, $HCrO_4^-(aq)$, and $Cr_2O_7^{2-}(aq)$ over a substantial range of temperatures. Now that the results of PALMER *et al.* are available, the ΔC_p° values calculated from the present direct measurements can be compared with their derived values, and comparisons of calculated $K = f(T)$ from this study with their direct results can also be made.

Because the chemical equilibria involving $CrO_4^{2-}(aq)$, $HCrO_4^-(aq)$, and $Cr_2O_7^{2-}(aq)$ are temperature dependent, the temperature increases inherent in calorimetric measurements of heat capacities lead to shifts in the speciation in the solutions under investigation. As previously shown in Chapter 4 and several investigations elsewhere, the resulting "relaxation contributions" to measured heat capacities can be quite large and must be considered in obtaining the desired standard state partial molar heat capacities for calculations of the type described above. Aqueous solutions containing Cr(VI) under the conditions of present interest introduce further complexities into the analysis of relaxational contributions because of the presence of coupled chemical equilibria.

In addition to calorimetric measurements, densimetric measurements on all of these same systems have been completed. These densities permit calculation of apparent molar volumes and thence partial molar volumes of solute species. The resulting partial molar volumes of Cr(VI) species can be used to obtain ΔV° values for the equilibria under present consideration. Finally, these ΔV° values can be used

in calculating $K = f(p)$, using the thermodynamic equation

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = \frac{-\Delta V^\circ}{RT} \tag{5.6}$$

5.2 Experimental

Water used for all solutions was first passed through an activated charcoal filter, then through a Milli-RO4/Milli-Q reagent grade mixed bed ion exchange system to achieve a final resistivity of 18MΩ cm or greater.

Standard NaCl solutions were prepared by mass from the salt (Fisher certified, ACS) after drying at 110°C for 24 hours. Potassium hydroxide (1M, certified solution) and perchloric acid (60%, certified ACS) were both obtained from Fisher and used without futher purification.

Three different potassium chromate stock solutions were prepared by mass and are labeled C1, C2, and C3. The first potassium chromate stock solution (C1) was prepared by mass from K_2CrO_4 (Fisher certified ACS, dried at 150°C for several hours) and 10^{-3} molal KOH. Some of the same sample of K_2CrO_4 from Fisher used to prepare C1 was recrystallized, dried at 150°C, and then used to prepare a second stock solution (C2) by mass with pure water. The third stock solution (C3) was prepared by mass from pure water and another sample of K_2CrO_4 (BDH certified ACS, dried at 110°C to constant mass). Other solutions were prepared by diluting C1 with 10^{-3} molal KOH and by diluting C2 and C3 with pure water; all dilutions were done on a mass basis.

Potassium dichromate (Fisher certified ACS, dried at 150° to constant mass) was dissolved in 10^{-5} molal $HClO_4$ to yield stock solution labeled D1. Another stock solution (D2) was prepared by dissolving some of the same sample of $K_2Cr_2O_7$ (freshly dried) in pure water. Both stock solutions were prepared by mass. Further solutions were prepared by diluting (by mass) D1 with 10^{-5}m $HClO_4$ and D2 with pure water.

Heat capacities were measured at 25.00 ± 0.01°C with a Picker flow microcalorimeter (PICKER *et al.*, 1971). The specific heat capacity of water was taken from KELL (1972), and had the value 4.1793 J $K^{-1}g^{-1}$. The heat capacities were corrected for very small unsymmetrical heat losses as described in Chapter 2 by the measurement

of the heat capacity of standard aqueous 1m NaCl solutions (DESNOYERS *et al.*, 1976). The calculated heat loss factor (f) for these studies was found to be 1.005 ± 0.001. Densities of all solutions were made relative to water at 25.00 ± 0.01°C with a Sodev O3D vibrating tube densimeter (PICKER *et al.*, 1974), which had been calibrated with water and a standard solution of NaCl. The density of water was taken from KELL (1967) and had the value 0.997047 g cm^{-3}, the density of the standard NaCl solution was taken from PICKER *et al.* (1974). Temperatures were controlled for the densimeter and calorimeter by separate Sodev CT-L circulating baths (constant to ± 0.001 °C). The temperatures of the baths and hence densimeter and calorimeter were measured with calibrated thermistors in the coolant lines.

5.3 Results

5.3.1 Solutions without added electrolyte: K_2CrO_4 (C2, C3) and $K_2Cr_2O_7$ (D2)

Results of calorimetric measurements of heat capacities and also the results of our measurements of densities of solutions can be related to the desired partial molar properties of solutes by way of apparent molar properties ($^{\phi}Y_2$) defined generally by

$$^{\phi}Y_2 = \frac{Y_{sol} - n_1 Y_1^{\circ}}{n_2} \tag{5.7}$$

in which Y_{sol} is the extensive property (volume or heat capacity) of a specified amount of solution, Y_1° is the same extensive property of one mole of pure solvent, and n_1 and n_2 are the amounts (moles) of solvent and solute, respectively.

For a "simple" solution such as NaCl in water it is then appropriate to express the composition dependence of $^{\phi}Y$ in terms of a Debye-Hückel equation of the form (see Chapter 2)

$$^{\phi}Y_2 = \bar{Y}_2^{\circ} + A_Y \omega I^{1/2} + B_Y I \tag{5.8}$$

in which $^{\phi}Y_2^{\circ}$ is the apparent molar property at infinite dilution (equal to the desired standard state partial molar property), A_Y is the Debye-Hückel limiting slope (BRADLEY and PITZER, 1979; ANANTHASWAMY and ATKINSON, 1984), ω is the "valence factor", I is the ionic strength, and B_Y is an adjustable parameter. The ionic strength, valence factor, and molality are related by

$$I = \omega m = \frac{1}{2} \sum m_i z_i^2 \tag{5.9}$$

The heat capacities and volumes of present interest cannot be analyzed in the way summarized above because of complications associated with mixed electrolytes and also because of "relaxation contributions" to the heat capacities as mentioned in the Introduction.

Analysis of data for these more complicated solutions can begin by rewriting eq. 5.7 as

$$^{\phi}Y_2^{exp} = \frac{Y_{sol} - n_1 Y_1^{\circ}}{n_{2,i}} \qquad (5.7a)$$

in which $n_{2,i}$ represents the stoichiometric or initial amount (moles) of solute dissolved in the specified amount of water. Here we emphasize that n_2 in eq. 5.7 refers to the number of moles of solute in the solution, while $n_{2,i}$ in eq. 5.7a refers to the stoichiometric number of moles of solid solute added to water to form the solution. For "simple" solutes such as NaCl, $n_2 = n_{2,i}$. But for the solutions of present interest, $n_2 \neq n_{2,i}$. Each mole of solid $K_2Cr_2O_7$ that is dissolved in water does not yield one mole of $Cr_2O_7^{2-}$(aq) ions because of equilibrium reactions that lead to formation of some other ions. The present primary experimental data is reported in terms of the apparent molar properties defined by eq. 5.7a in which the superscript *exp* is intended to emphasize that these quantities have come directly from results of the calorimetric and densimetric measurements in combination with stoichiometric compositions of solutions. No chemical equilibrium calculations that lead to a description of solutions in terms of specified chemical species have yet been done.

Equations that further relate the defined eq. 5.7a experimental apparent molar properties to heat capacities and densities and to stoichiometric molalities of solutions are

$$^{\phi}V_2^{exp} = \frac{\dfrac{1 + m_{2,i}M_2}{d_{sol}} - \dfrac{1}{d_1^{\circ}}}{m_{2,i}} \qquad (5.10)$$

and

$$^{\phi}C_{p,2}^{exp} = \frac{c_{p,sol}(1 + m_{2,i}M_2) - c_{p,1}^{\circ}}{m_{2,i}} \qquad (5.11)$$

Here $c_{p,sol}$ and d_{sol}, $c_{p,1}^{\circ}$ and d_1° are the heat capacity and density of the solution and water, respectively, and M_2 is the solute's molecular weight. Experimental apparent molar properties along with the direct experimentally measured quantities $[c_{p,sol}d_{sol}/(c_{p,1}^{\circ}d_1^{\circ}) - 1]$ and $(d_{sol} - d_1^{\circ})$ are given in Table 5.1. The apparent molar

Table 5.1: Experimental apparent molar properties for K_2CrO_4 (C2, C3) and $K_2Cr_2O_7$ (D2).

$m_{2,i}$ (mol kg^{-1})	$10^3(d_{sol} - d_1^\circ)$ (g cm^{-3})	ϕV^{exp} (cm^3 mol^{-1})	$-10^3\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	ϕC_p^{exp} (J K^{-1}mol^{-1})
		K_2CrO_4(C2)		
0.36676	54.037	44.17	27.59	−137.15
0.36676	54.018	44.22	27.48	−135.63
0.25372	37.821	43.18	20.01	−155.04
0.23792	37.821	43.00	18.87	−157.50
0.17836	26.825	42.34	14.55	−168.95
0.11535	17.498	41.45	9.707	−182.54
0.066662	10.184	40.68	5.785	−196.06
0.041187	6.319	40.19	3.639	−204.38
		K_2CrO_4(C3)		
0.49694	72.498	44.76		
0.49694	72.533	44.70	35.56	−121.10
0.37753	55.779	43.70	28.26	−137.60
0.37753	55.756	43.76	28.33	−138.16
0.29578	44.050	43.06	22.95	−150.75
0.23735	35.573	42.49	18.90	−160.81
0.18352	27.679	41.90	14.99	−171.23
0.10588	16.132	40.84	8.987	−187.97
0.053230	8.177	39.93	4.679	−203.74
		$K_2Cr_2O_7$(D2)		
0.29268	56.488	95.50	26.22	11.01
0.24217	47.058	95.10	22.06	4.71
0.20539	40.114	94.79	18.93	0.16
0.16725	32.848	94.39	15.62	−5.15
0.14723	28.996	94.21	13.82	−7.34
0.111313	22.408	93.71	10.67	−10.01
0.074353	14.818	93.20	7.037	−12.06
0.037747	7.567	92.71	3.536	−8.60

properties listed in Table 5.1 must undergo further calculations to obtain heat capacities and volumes for the desired species as described later.

5.3.2 Solutions with added electrolyte: K_2CrO_4 (C1), $K_2Cr_2O_7$ (D1)

Solutions of K_2CrO_4 (C1) and $K_2Cr_2O_7$ (D1) contained additional potassium hydroxide and perchloric acid, respectively. The presence of this added hydroxide and acid in these solutions must be accounted for in analyzing the heat capacities and volumes that come directly from the calorimetric and densimetric measurements, that is done by using Young's rule (YOUNG and SMITH, 1954). Young's rule results in definition of "mean" apparent molar properties of a solution that contains x solutes by

$$^{\Phi}Y^{mean} = \frac{Y_{sol} - n_1 Y_1^{\circ}}{\sum_{j=2}^{x} n_j} \tag{5.12}$$

where Y_{sol} is the extensive property of a specified quantity of solution, Y_1° is the property of one mole of water, and n_1 and n_j are the stoichiometric number of moles of water and solute j in the specified quantity of solution.

Young's rule can be expressed for the systems of present interest by

$$^{\Phi}Y^{mean} = F_2{}^{\phi}Y^{exp} + F_3{}^{\phi}Y_3 + \delta \tag{5.13}$$

where δ is an excess mixing term, $F_j = m_j / \sum m_j$, and the apparent molar properties $^{\phi}Y^{exp}$ and $^{\phi}Y_3$ both pertain to the total ionic strength of the solution. Because the concentration of added KOH and $HClO_4$ is very small, it is justified to take $\delta = 0$ (YOUNG and SMITH, 1954). The equations that define mean apparent molar volumes and heat capacities for solutions containing two solutes are given below.

$$^{\Phi}V^{mean} = \frac{\dfrac{1 + m_{2,i}M_2 + m_3M_3}{d_{sol}} - \dfrac{1}{d_1^{\circ}}}{m_{2,i} + m_3} \tag{5.14}$$

$$^{\Phi}C_p^{mean} = \frac{c_{p,sol}(1 + m_{2,i}M_2 + m_3M_3) - c_{p,1}^{\circ}}{m_{2,i} + m_3} \tag{5.15}$$

Here all symbols have the same meaning as above, and m_3 is the molality of the added electrolyte. These mean apparent molar properties are listed in Table 5.2 along with the experimentally measured quantities $[c_{p,sol}d_{sol}/(c_{p,1}^{\circ}d_1^{\circ}) - 1]$ and $(d_{sol} - d_1^{\circ})$.

Table 5.2: "Mean" Apparent Molar Properties for K_2CrO_4 (C1) and $K_2Cr_2O_7$ (D1).

$m_{2,i}$ (mol kg^{-1})	$10^3(d_{sol} - d_1^\circ)$ (g cm^{-3})	$^\phi V^{exp}$ (cm^3 mol^{-1})	$-10^3\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	$^\phi C_p^{exp}$ (J K^{-1}mol^{-1})
		K_2CrO_4(C1), KOH = 1.003×10^{-3}m		
0.53441	77.619	45.16	37.65	−114.76
0.40987	60.270	44.20	30.26	−131.31
0.31029	46.096	43.36	23.93	−147.02
0.25490	38.103	42.81	20.14	−156.25
0.20469	30.795	42.19	16.58	−166.29
0.15488	23.453	41.55	12.86	−176.16
0.10618	16.194	40.83	9.081	−187.80
0.049394	7.654	38.94	4.400	−205.76
		$K_2Cr_2O_7$(D1), $HClO_4 = 9.43 \times 10^{-6}$m		
0.35341	67.570	96.21	30.92	20.40
0.29064	56.019	95.78	26.02	12.04
0.24554	47.610	94.45	22.36	5.67
0.20149	39.310	95.05	18.53	1.81
0.15099	29.690	94.45	14.12	−5.49
0.095288	18.886	93.90	9.028	−10.79
0.050920	10.167	93.26	4.820	−11.43
0.022347	4.503	91.97	2.045	−2.41

Expressions for the apparent molar volumes and heat capacities of KOH and $HClO_4$ were taken from ROUX *et al.* (1984) and from Chapter 2, respectively. The calculated values of ${}^{\phi}Y^{exp}$ and contributions from the added electrolyte are given in Table 5.3 for stock solutions (C1) and (D1). As is evident from Table 5.3, the contribution of the added $HClO_4$ to the experimental apparent molar volumes and heat capacities for $K_2Cr_2O_7$ solutions is small enough to ignore in subsequent calculations. The added KOH in solutions containing K_2CrO_4 was very small (10^{-3}m), but large enough to prevent any appreciable formation of the bichromate ($HCrO_4^-$) anion (PALMER *et al.*, 1987). Subsequently, all of the chromium(VI) present in these solutions can be considered to be in the form CrO_4^{2-}(aq). However, as mentioned earlier, the experimental apparent molar volumes for solutions containing $K_2Cr_2O_7$ must still be treated with consideration of the speciation reactions, and the experimental apparent molar heat capacities must be treated for speciation and chemical relaxation.

5.3.3 Speciation Calculations

The amounts of all species present at equilibrium in all of the solutions investigated here were calculated from the equilibrium constants from PALMER *et al.* (1987), using auxiliary data from BUSEY and MESMER (1978) [dissociation constant of H_2O(l)] and LIU and LINDSAY (1972) [osmotic coefficient data for NaCl(aq)]. The calculated equilibrium molalities of each species present in the solutions are listed in Tables 5.4 and 5.5. The equilibrium quotients (Q) associated with equilibria 5.1 and 5.4 at specific ionic strengths equal to prepared solutions are also included.

5.4 Relaxation contributions

The total enthalpy of a homogeneous system containing k components can be defined (MAINS *et al.*, 1984) as

$$H = \sum_k n_k H_k \tag{5.16}$$

where n_k and H_k are the numbers of moles and partial molar enthalpies of the k'th component. Since the heat capacity is the constant pressure derivative of the

Table 5.3: Young's rule analysis of "mean" apparent molar properties of K_2CrO_4 (C1) and $K_2Cr_2O_7$.

$m_{2,i}$ (mol kg^{-1})	$\frac{m_{2,i}+m_3}{m_{2,i}}\Phi V^{mean}$ (cm^3 mol^{-1})	$\frac{m_3}{m_{2,i}}\phi V_3$ (cm^3 mol^{-1})	${}^{\phi}V_2^{exp}$ (cm^3 mol^{-1})	$\frac{m_{2,i}+m_3}{m_{2,i}}\Phi C_p^{mean}$ (J K^{-1}mol^{-1})	$\frac{m_3}{m_{2,i}}\phi C_{p,3}$ (J K^{-1}mol^{-1})	${}^{\phi}C_{p,2}^{exp}$ (J K^{-1}mol^{-1})
			K_2CrO_4(C1)			
0.53441	45.25	0.02	45.23	−115.0	−0.13	−114.8
0.40987	44.30	0.02	44.29	−131.6	−0.19	−131.4
0.31029	43.50	0.03	43.47	−147.5	−0.27	−147.2
0.25490	42.98	0.03	42.95	−156.9	−0.35	−156.5
0.20469	42.39	0.03	42.36	−167.1	−0.46	−166.6
0.15488	41.82	0.04	41.78	−177.3	−0.65	−176.7
0.10618	41.22	0.06	41.16	−189.6	−1.00	−186.6
0.049394	39.73*	0.12	39.62	−209.9	−2.34	−207.6
			$K_2Cr_2O_7$(D1)			
0.35341	96.21	0.001	96.21	20.4	2×10^{-4}	20.4
0.29064	95.79	0.001	95.79	12.0	2×10^{-4}	12.0
0.24554	95.45	0.002	95.45	5.7	1×10^{-4}	5.7
0.20149	95.06	0.002	95.06	1.8	1×10^{-6}	1.8
0.15099	94.45	0.003	94.45	−5.5	-2×10^{-4}	−5.5
0.095288	93.91	0.004	93.91	−10.8	-8×10^{-4}	−10.8
0.050920	93.28	0.008	93.27	−11.4	-2×10^{-3}	−11.4
0.022347	92.08	0.019	91.99	−2.4	-7×10^{-3}	−2.4

* not used in least squares fits.

Table 5.4: Speciation of K_2CrO_4 solutions (C2, C3)*

$m_{2,i}$ (mol kg^{-1})	$m_2(K_2CrO_4)$ (mol kg^{-1})	$m_3(K[HCrO_4])$ $10^{-5} \times$ (mol kg^{-1})	I (mol kg^{-1})	$\log Q_1$	$\log Q_{19}$
		K_2CrO_4(C2)			
0.36676	0.36670	5.78	1.1003	−8.034	−14.01
0.25372	0.25367	5.21	0.7612	−7.966	−13.90
0.23792	0.23787	5.11	0.7138	−7.955	−13.89
0.17836	0.17831	4.67	0.5351	−7.908	−13.82
0.11535	0.11531	4.05	0.3461	−7.843	−13.74
0.066662	0.066628	3.35	0.2000	−7.772	−13.65
0.041187	0.041159	2.80	0.1236	−7.717	−13.59
		K_2CrO_4(C3)			
0.49694	0.49688	6.25	1.4908	−8.098	−14.11
0.37753	0.37747	5.83	1.1326	−8.040	−14.02
0.29578	0.29572	5.44	0.8873	−7.994	−13.94
0.23735	0.23730	5.10	0.7121	−7.955	−13.89
0.18352	0.18347	4.71	0.5506	−7.913	−13.83
0.10588	0.10584	3.94	0.3176	−7.831	−13.72
0.053230	0.053199	3.09	0.1597	−7.745	−13.62

* $\log Q_1$ and $\log Q_{19}$ refer to reactions represented by eqs. 5.1 and 5.19, respectively.

Table 5.5: Speciation of $K_2Cr_2O_7$ solutions (D1, D2)*

$m_{2,i}$ (mol kg^{-1})	$m_2(K_2Cr_2O_7)$ (mol kg^{-1})	$m_3(K[HCrO_4])$ (mol kg^{-1})	$m_4(KH[CrO_4])$ 10^{-4}(mol kg^{-1})	I (mol kg^{-1})	$\log Q_1$	$\log Q_{19}$
			$K_2Cr_2O_7$(D1)			
0.35341	0.32647	0.05355	3.28	1.0339	−8.022	−13.99
0.29064	0.26584	0.04929	3.06	0.8477	−7.985	−13.93
0.24554	0.22243	0.04592	2.87	0.7141	−7.955	−13.89
0.20149	0.18022	0.04228	2.66	0.5837	−7.922	−13.84
0.15099	0.13213	0.03748	2.36	0.4346	−7.876	−13.78
0.09529	0.07979	0.03081	1.95	0.2708	−7.810	−13.70
0.05092	0.03921	0.02326	1.48	0.1413	−7.732	−13.60
0.02235	0.01457	0.01546	1.03	0.05947	−7.648	−13.51
			$K_2Cr_2O_7$(D2)			
0.29268	0.26781	0.04944	3.06	0.8538	−7.987	−13.93
0.24217	0.21920	0.04566	2.85	0.7041	−7.953	−13.88
0.20539	0.18394	0.04262	2.68	0.5953	−7.925	−13.84
0.16725	0.14757	0.03912	2.46	0.4826	−7.892	−13.80
0.14723	0.12857	0.03708	2.34	0.4235	−7.872	−13.77
0.11313	0.09644	0.03317	2.09	0.3231	−7.834	−13.72
0.07435	0.06045	0.02763	1.75	0.2095	−7.777	−13.66
0.03775	0.02759	0.02018	1.30	0.1033	−7.699	−13.57

* $\log Q_1$ and $\log Q_{19}$ refer to reactions represented by eqs. 5.1 and 5.19, respectively.

enthalpy, differentiation of eq 5.16 leads to

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p = \sum_k n_k \left(\frac{\partial H_k}{\partial T}\right)_p + \sum_k H_k \left(\frac{\partial n_k}{\partial T}\right)_p \tag{5.17}$$

The first term in this expression represents the compositional heat capacity (the only term present in single component single phase systems) and the second term represents the contribution to the heat capacity from the shift in the number of moles of each species present. This second term is the relaxation contribution to calorimetrically measured heat capacities and was discussed in detail for the ionization of bisulphate ion in the preceding Chapter.

Several elegant treatments and discussions of relaxation effects (MAINS *et al.*, 1984; WOOLLEY and HEPLER, 1977; LARSON *et al.*, 1982; BARBERO *et al.*, 1983) have been presented mostly concerned with the relaxation contributions in systems containing a single dissociating (or associating) solute. The relationship of the shift in the equilibrium [represented by $(\partial\alpha/\partial T)_p$] to measured apparent molar heat capacities of the type presented here is

$${}^{\phi}C_p^{rel} = \Delta H_{rxn} \left(\frac{\partial \alpha}{\partial T}\right)_p \tag{5.18}$$

for solutions with a single dissociation (or association) equilibrium. Here ΔH_{rxn} represents the enthalpy change for the reaction of interest at the total equilibrium ionic strength of the solution. The relationship of these enthalpies of reaction at finite ionic strengths to the standard state enthalpies of reaction (denoted by ΔH°) is discussed in Chapter 4.

5.4.1 K_2CrO_4 + KOH (C1)

Two of the reactions that can be written to describe the speciation in aqueous solutions containing chromate ion are

$$CrO_4^{2-}(aq) + H_2O(l) = HCrO_4^{-}(aq) + OH^{-}(aq) \tag{5.1}$$

and

$$2CrO_4^{2-}(aq) + H_2O(l) = Cr_2O_7^{2-}(aq) + 2OH^{-}(aq) \tag{5.19}$$

The magnitudes of the equilibrium constants associated with the reactions represented by eqs. 5.1 and 5.19 show that only the reaction described by eq. 5.1 is

required for speciation calculations in aqueous solutions prepared from K_2CrO_4 and water (no significant amounts of acid). Consideration of eq. 5.1 leads to the following equilibrium molalities in solutions prepared from $m_{2,i}$ (K_2CrO_4) and water:

$$[CrO_4^{2-}] = (1-\alpha)m_{2,i} \tag{5.20}$$

$$[HCrO_4^-] = \alpha m_{2,i} \tag{5.21}$$

$$[OH^-] = \alpha m_{2,i} \tag{5.22}$$

The relaxation contributions to the experimental apparent molar heat capacities for solutions of potassium chromate in water (for the reaction represented by eq. 5.1) are given by:

$${}^{\phi}C_{p,\alpha}^{rel} = \Delta H_1 \left(\frac{\partial \alpha}{\partial T}\right)_p \tag{5.23}$$

The term represented by $(\partial\alpha/\partial T)_p$ was calculated from

$$\left(\frac{\partial \alpha}{\partial T}\right)_p = \frac{Q_1 \Delta H_1 (1-\alpha)}{RT^2(2\alpha m_{2,i} + Q_1)} \tag{5.24}$$

where Q_1 and ΔH_1 are the equilibrium quotient and enthalpy of the reaction represented by eq 5.1 at the ionic strength of the solution. The contributions of chemical relaxation to the solutions of potassium chromate solutions dissolved in pure water (stock solutions C2 and C3) were calculated from eq. 5.24 using Q_1 values from PALMER *et al.* (1987), and ΔH_f° values[2] that are listed in Table 5.6. The results of all of these relaxation calculations are given in Table 5.7.

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[2]It appears that the best ΔH° values and derived ΔH_f° values for CrO_4^{2-}(aq), $HCrO_4^-$(aq), and $Cr_2O_7^{2-}$(aq) are those cited by DELLIEN *et al.* (1976), based largely on the results of calorimetric measurements. The more recent ΔH° and ΔH (referring to specified ionic strengths) values calculated by PALMER *et al.* (1987) from the temperature dependence of their equilibrium constants (quotients) appear to be less accurate than those from DELLIEN *et al.* (1976), but these ΔH values have the advantage of applying to finite ionic strengths of our solutions rather than to infinite dilution as do the ΔH° values. Consideration of probable uncertainties in all of these values and in estimated enthalpies of dilution that might be used to obtain ΔH values from ΔH° values has led to the use of ΔH_1° in eq. 5.24. This approach means that the effect of temperature on activity coefficients is ignored. Some of the error introduced by the use of ΔH° instead of ΔH is eliminated by extrapolations to infinite dilution, where these two enthalpies become equal to each other. All of these uncertainties have been considered in our estimates of total uncertainties in derived standard state partial molar heat capacities.

Table 5.6: Standard state enthalpy values for selected aqueous species at 25°C.

Species	$\Delta H^{\circ}_{f,298}$ (kJ mol^{-1})	Reference
$H^+(aq)$	0	
$H_2O(l)$	−285.83	WAGMAN *et al.* (1982)
$OH^-(aq)$	−229.994	WAGMAN *et al.* (1982)
$HCrO_4^-(aq)$	−878.22	DELLIEN *et al.* (1976)
$CrO_4^{2-}(aq)$	−881.15	DELLIEN *et al.* (1976)
$Cr_2O_7^{2-}(aq)$	−1490.3	DELLIEN *et al.* (1976)

Table 5.7: Relaxation contributions for K_2CrO_4 (C2, C3) solutions.

$m_{2,i}$ (mol kg^{-1})	$10^4\alpha$	$10^6\left(\frac{\partial\alpha}{\partial T}\right)_p$ (K^{-1})	${}^{\phi}C_p^{rel}$ (J K^{-1}mol^{-1})
		K_2CrO_4(C2)	
0.36676	1.577	5.723	0.30
0.25372	2.052	7.432	0.39
0.23792	2.147	7.771	0.41
0.17836	2.620	9.464	0.50
0.11535	3.513	12.67	0.67
0.066662	5.023	18.06	0.96
0.041187	6.808	24.47	1.29
		K_2CrO_4(C3)	
0.49694	1.258	4.572	0.24
0.37753	1.544	5.600	0.30
0.29578	1.841	6.663	0.35
0.23735	2.150	7.776	0.41
0.18352	2.569	9.272	0.49
0.10588	3.718	13.41	0.71
0.053230	5.796	20.85	1.10

5.4.2 $K_2Cr_2O_7$

The equilibrium properties of aqueous solutions prepared by dissolving a dichromate salt in water can be described accurately in terms of two equilibria that are represented by

$$Cr_2O_7^{2-}(aq) + H_2O(l) = 2CrO_4^{2-}(aq) + 2H^+(aq) \tag{5.2}$$

and

$$CrO_4^{2-}(aq) + H^+(aq) = HCrO_4^-(aq) \tag{5.25}$$

One simple (inadequate, as discussed below) approach to the relaxation contribution to heat capacities is to combine eq. 5.2 with eq. 5.25 to obtain

$$Cr_2O_7^{2-}(aq) + H_2O(l) = 2HCrO_4^-(aq) \tag{5.3}$$

Consideration of the equilibrium represented by eq. 5.3 then leads to

$$\left(\frac{\partial \alpha}{\partial T}\right)_p = \frac{Q_3 \Delta H_3 (1-\alpha)}{RT^2(8\alpha m_{2,i} + Q_3)} \tag{5.26}$$

that might be used in calculating the relaxation contribution to the heat capacity. Unfortunately for the sake of a relatively simple treatment of chemical relaxation, eq. 5.3 and 5.26 are inadequate because non-negligible fractions of $HCrO_4^-(aq)$ are dissociated into $H^+(aq)$ and $CrO_4^{2-}(aq)$. Similarly, an analysis based solely on the equilibrium represented by eq. 5.2 is inadequate because non-negligible fractions of $CrO_4^{2-}(aq)$ are associated with $H^+(aq)$ as given by eq. 5.25. The complications associated with the coupled equilibria represented by eq. 5.2 and 5.25 must be considered including all three of the Cr(VI) species present.

The fraction of stoichiometric $Cr_2O_7^{2-}(aq)$ that reacts according to eq. 5.2 is denoted by α and similarly β is used to represent the fraction of $CrO_4^{2-}(aq)$ that subsequently reacts according to eq. 5.25. The equilibrium molalities of the various species are defined in terms of α, β, and the stoichiometric molality of dichromate ($m_{2,i}$) as follows:

$$[Cr_2O_7^{2-}] = (1-\alpha)m_{2,i} \tag{5.27}$$

$$[CrO_4^{2-}] = 2(\alpha-\beta)m_{2,i} \tag{5.28}$$

$$[HCrO_4^-] = 2\beta m_{2,i} \tag{5.29}$$

$$[H^+] = 2(\alpha-\beta)m_{2,i} \tag{5.30}$$

The total contribution of chemical relaxation to the solutions of potassium dichromate is the sum of the individual contributions from each of the equilibria represented by eqs. 5.2 and 5.25 as in

$$^{\phi}C_{p,tot}^{rel} = {}^{\phi}C_{p,\alpha}^{rel} + {}^{\phi}C_{p,\beta}^{rel} \tag{5.31}$$

where $^{\phi}C_{p,\alpha}^{rel}$ and $^{\phi}C_{p,\beta}^{rel}$ are given by:

$$^{\phi}C_{p,\alpha}^{rel} = \Delta H_2 \left(\frac{\partial \alpha}{\partial T}\right)_p \tag{5.32}$$

and

$$^{\phi}C_{p,\beta}^{rel} = \Delta H_{25} \left(\frac{\partial \alpha}{\partial T}\right)_p \tag{5.33}$$

After differentiation and much mathematical manipulation the following expressions for $(\partial\alpha/\partial T)_p$ and $(\partial\alpha/\partial T)_p$ are obtained:

$$\left(\frac{\partial \alpha}{\partial T}\right)_p = \frac{\frac{1}{RT^2}\left\{\frac{Q_2 \Delta H_2 (1-\alpha)[1+4m_{2,i}Q_{25}(\alpha-\beta)]}{64m_{2,i}^3(\alpha-\beta)^3} + 2m_{2,i}(\alpha-\beta)^2 Q_{25}\Delta H_{25}\right\}}{\frac{[Q_2 + 64M_{2,i}^3(\alpha-\beta)^3][1+4m_{2,i}Q_{25}(\alpha-\beta)]}{64m_{2,i}^3(\alpha-\beta)^3} - 4m_{2,i}Q_{25}(\alpha-\beta)} \tag{5.34}$$

$$\left(\frac{\partial \beta}{\partial T}\right)_p = \frac{\left(\frac{\partial \alpha}{\partial T}\right)_p [Q_2 + 64m_{2,i}^3(\alpha-\beta)^3] - \frac{(1-\alpha)Q_2\Delta H_2}{RT^2}}{64m_{2,i}^3(\alpha-\beta)^3} \tag{5.35}$$

Here Q_2 and ΔH_2 are the equilibrium quotient and enthalpy change associated with the reaction represented by eq. 5.2 and Q_{25} and ΔH_{25} are similar quantities for the reaction represented by by eq. 5.25. The equilibrium data used in all of these calculations were taken from PALMER *et al.* (1987) and the enthalpies were derived from ΔH_f° values for individual species as listed in Table 5.6. The calculated values of the contributions of chemical relaxation to the measured heat capacities of solutions containing potassium dichromate are given in Table 5.8.

5.5 Standard state properties

The apparent molar properties of all of the species reported here are successfully represented to moderate molalities by Debye-Hückel expressions of the form

$$^{\phi}Y_2 = \bar{Y}_2^{\circ} + A_Y \omega I^{1/2} + B_Y I \tag{5.8}$$

Table 5.8: Relaxation contributions to heat capacity measurements for $K_2Cr_2O_7$ solutions.

$m_{2,i}$ (mol kg^{-1})	$10^2\alpha$	$10^2\beta$	$10^4\left(\frac{\partial\alpha}{\partial T}\right)_p$ (K^{-1})	$10^4\left(\frac{\partial\beta}{\partial T}\right)_p$ (K^{-1})	${}^{\phi}C_{p,\alpha}^{rel}$ (J K^{-1}mol^{-1})	${}^{\phi}C_{p,\beta}^{rel}$ (J K^{-1}mol^{-1})	${}^{\phi}C_{p,tot}^{rel}$ (J K^{-1}mol^{-1})
				$K_2Cr_2O_7$(D1)			
0.35341	7.577	7.623	9.661	9.681	13.36	2.84	16.20
0.29064	8.533	8.480	10.84	10.82	14.99	3.17	18.16
0.24554	9.410	9.352	11.87	11.85	16.42	3.47	19.89
0.20149	10.56	10.49	13.22	13.19	18.29	3.87	22.16
0.15099	12.49	12.41	15.49	15.45	21.42	4.53	25.95
0.09529	16.27	16.17	19.70	19.66	27.24	5.76	33.00
0.05092	22.99	22.84	26.52	26.46	36.68	7.75	44.43
0.02235	34.82	34.59	36.49	36.41	50.47	10.67	61.14
				$K_2Cr_2O_7$(D2)			
0.29268	8.498	8.446	10.79	10.77	14.92	3.15	18.07
0.24217	9.486	9.427	11.96	11.93	16.54	3.50	20.04
0.20539	10.44	10.38	13.12	13.09	18.14	3.83	21.97
0.16725	11.77	11.69	14.58	14.55	20.16	4.26	24.42
0.14723	12.67	12.59	15.74	15.71	21.77	4.60	26.37
0.11313	14.75	14.66	17.95	17.91	24.83	5.25	30.08
0.07435	18.70	18.58	22.21	22.16	30.72	6.49	37.21
0.037747	26.90	26.73	30.12	30.05	41.65	8.81	50.46

in which all quantities were previously defined. The Debye-Hückel slopes used were $A_C = 32.783$ J $K^{-1}kg^{1/2}mol^{-3/2}$ and $A_V = 1.8743$ $cm^3kg^{1/2}mol^{-3/2}$, taken from ANANTHASWAMY and ATKINSON (1984).

5.5.1 K_2CrO_4 (C1)

The potassium chromate solutions represented by (C1) were prepared by dissolving solid K_2CrO_4 in dilute KOH sufficient to avoid formation of any significant amounts of the bichromate species. These solutions may be regarded as having only one chromium(VI) species, namely $CrO_4^{2-}(aq)$. Equations of type 5.8 were fitted to the ${}^{\phi}Y_2$ values for K_2CrO_4 (C1) that are listed in Table 5.3. These fits resulted in definition of the values ${}^{\phi}Y_2^{\circ}$ and B_Y and corresponding statistical uncertainties as listed in Table 5.9. Values of ${}^{\phi}Y_2$ minus the Debye-Hückel limiting law are plotted in Figure 5.1 along with data calculated from the solutions that are represented as (C2) and (C3) that are discussed later.

5.5.2 $K_2Cr_2O_7$ (D1, D2)

As previously mentioned, it is necessary to consider $Cr_2O_7^{2-}(aq)$, $HCrO_4^{-}(aq)$, and $CrO_4^{2-}(aq)$ ions in our solutions of $K_2Cr_2O_7$. Because our measurements on slightly alkaline solutions of K_2CrO_4 have resulted in heat capacity and volumetric properties of $CrO_4^{2-}(aq)$, the measurements on stock solutions D1 and D2 are intended for evaluation of properties for the other two Cr(VI) ions.

To begin the present analysis, estimated properties of the hypothetical solute designated here as (K^+, H^+, CrO_4^{2-}) with molality m_4 were obtained from the scheme

$$ {}^{\phi}Y(K^+,\ H^+,\ CrO_4^{2-}) = {}^{\phi}Y(K_2CrO_4) - {}^{\phi}Y(KCl) + {}^{\phi}Y(HCl) \qquad (5.36) $$

Values of ${}^{\phi}Y$ for aqueous KCl and HCl were selected from DESNOYERS *et al.* (1976), FORTIER *et al.* (1974), and ALLRED and WOOLLEY (1981). For aqueous K_2CrO_4 ${}^{\phi}Y$ values derived from Table 5.9 (rather than similar values derived later) were used to maximize the internal consistency of our results.

The relationships between the defined "experimental" apparent molar volumes and apparent molar heat capacities and the same properties of single electrolytes

Table 5.9: Standard state (infinite dilution) partial molar heat capacities, volumes and B_Y parameters at 25.0°C.*

Solute	${}^{\phi}V_2^{\circ}$ ($cm^3 mol^{-1}$)	B_V ($cm^3 kg\ mol^{-2}$)	${}^{\phi}C_{p,2}^{\circ}$ ($JK^{-1}mol^{-1}$)	B_C ($J\ kg\ K^{-1}mol^{-2}$)
K_2CrO_4(C1)	37.91 ± 0.02	0.120 ± 0.03	-245.9 ± 0.2	4.13 ± 0.3
K_2CrO_4(C2)	38.15 ± 0.02	0.131 ± 0.04	-241.8 ± 0.6	1.42 ± 0.8
K_2CrO_4(C3)	37.64 ± 0.03	0.134 ± 0.03	-245.2 ± 0.4	2.06 ± 0.5
$K_2Cr_2O_7$(D1, D2)	91.1 ± 0.3	-0.55 ± 0.3	-105.0 ± 1.4	1.9 ± 1.5
K[HCrO4]	54.6 ± 0.5	(0 ± 1)	14.7 ± 2	(30 ± 10)

* The $\pm$ values are the statistical uncertainties (standard deviations) associated with the fit of eq. 5.8 to the experimental results. Total uncertainties are larger than these $\pm$ values, as discussed in the text.

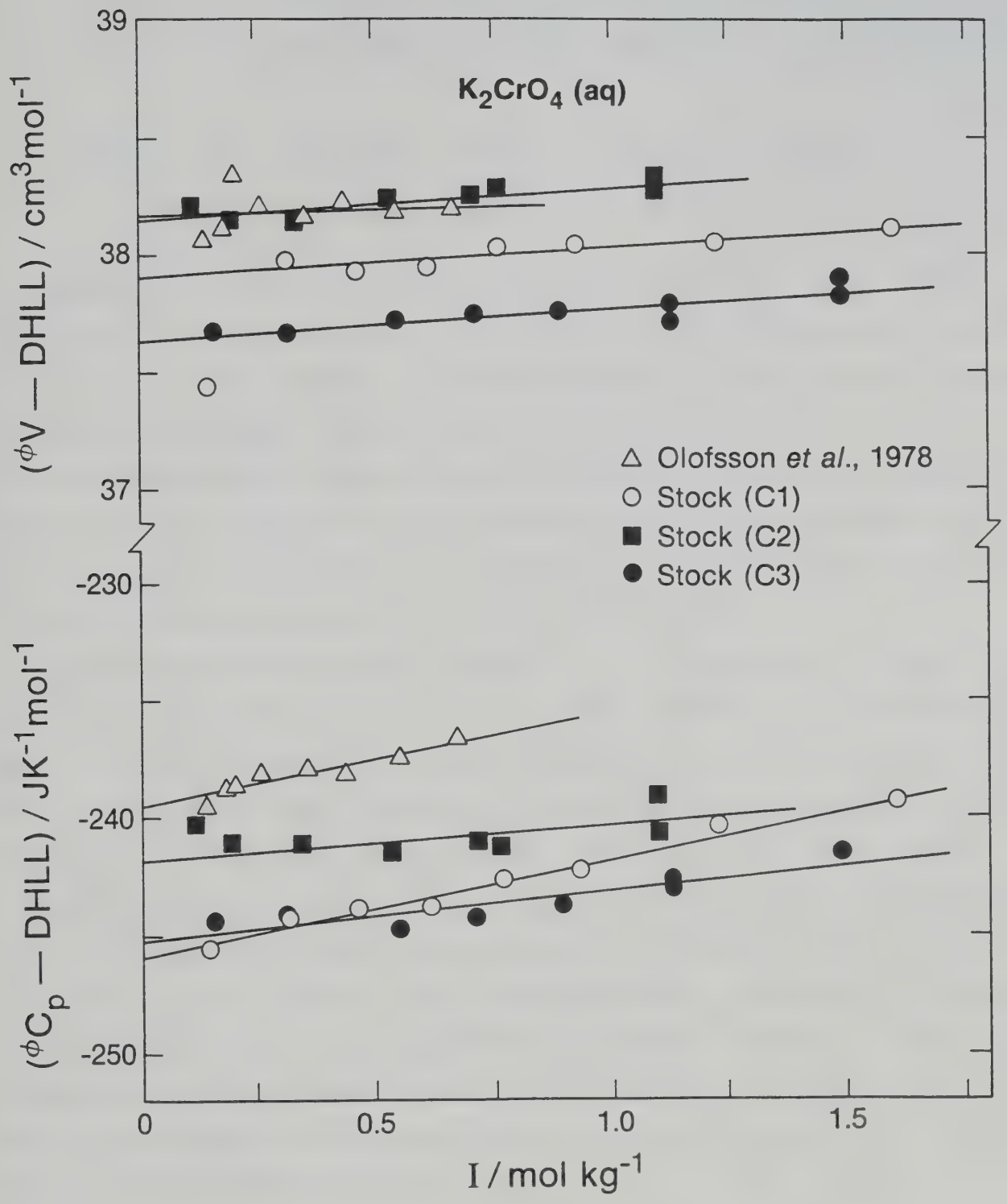

Figure 5.1: Plots of ${}^{\phi}Y_2$ minus the Debye-Hückel limiting law term (DHLL) for K_2CrO_4 solutions after correction for speciation and relaxation.

are

$$
\begin{aligned}
{}^{\phi}V^{exp} &= (1-\alpha){}^{\phi}V_2(2K^+,\ Cr_2O_7^{2-}) + 2\beta{}^{\phi}V_3(K^+,\ HCrO_4^-) + \\
&\quad 2(\alpha-\beta){}^{\phi}V_4(K^+,\ H^+,\ CrO_4^{2-}) - \alpha\bar{V}^{\circ}(H_2O) \qquad (5.37)
\end{aligned}
$$

$$
\begin{aligned}
{}^{\phi}C_p^{exp} &= (1-\alpha){}^{\phi}C_{p,2}(2K^+,\ Cr_2O_7^{2-}) + 2\beta{}^{\phi}C_{p,3}(K^+,\ HCrO_4^-) + \\
&\quad 2(\alpha-\beta){}^{\phi}C_{p,4}(K^+,\ H^+,\ CrO_4^{2-}) - \bar{C}_p^{\circ}(H_2O) + {}^{\phi}C_p^{rel} \qquad (5.38)
\end{aligned}
$$

Simultaneous least squares analysis of eqs. 5.37 and 5.8 for volumes leads to $\bar{V}_2^{\circ}$ and B_V values for $(2K^+,\ Cr_2O_7^{2-})$ and for $(K^+,\ HCrO_4^-)$. Similar least squares analysis of eqs. 5.38 and 5.8 for heat capacities leads to $\bar{C}_p^{\circ}$ and B_C values for both of these same electrolytes. Required values for the properties of water ($\bar{V}^{\circ}$ and $\bar{C}_p^{\circ}$) were taken as listed from Table 5.6. This kind of analysis in terms of four adjustable parameters results in slight statistical overfitting of the experimental results, that has led us to reduce the number of adjustable parameters by estimating values of B_V and B_C for the lowest molality electrolyte, $(K^+ + HCrO_4^-)$.

The B_V values for various other "similar" (+1, −1) electrolytes as reported by DESNOYERS *et al.* (1976), BARBERO *et al.* (1983), and ROUX *et al.* (1978) range from -1.4 to 1.3 $cm^3 kg\ mol^{-2}$. The B_C values for these same electrolytes range from 18 to 39 J $kg\ K^{-1} mol^{-2}$. Using these values as guides, the values $B_V = 0 \pm 1$ $cm^3 kg\ mol^{-2}$ and $B_C = 30 \pm 10$ J $kg\ K^{-1} mol^{-2}$ were estimated for $(K^+,\ HCrO_4^-)$.

Results of the fits of eq. 5.37, 5.38, and corresponding versions of eq. 5.8, using the B_V and B_C values specified above, are summarized in Table 5.9. Letting the values of B_V and B_C for $(K^+,\ HCrO_4^-)$ vary over the specified $\pm$ ranges leads to changes of less than 2 J $K^{-1} mol^{-1}$ and 0.2 $cm^3 mol^{-1}$ in $\bar{C}_p^{\circ}$ and $\bar{V}^{\circ}$ for $(2K^+,\ Cr_2O_7^{2-})$ and to slightly larger changes in these values for $(K^+,\ HCrO_4^-)$. Graphs in Figures 5.2 and 5.3 show the results of these calculations,[3] in which the straight lines are based on the parameters listed in Table 5.9.

[3]The plotted quantities were generated by appropriate rearrangement of eq. 5.37 and 5.38 and substitution of expressions derived from eq. 5.8 for $(2K^+,\ Cr_2O_7^{2-})$ and $(K^+,\ HCrO_4^-)$. As evident from the above discussion, the calculations and plots for these two solutes are not independent.

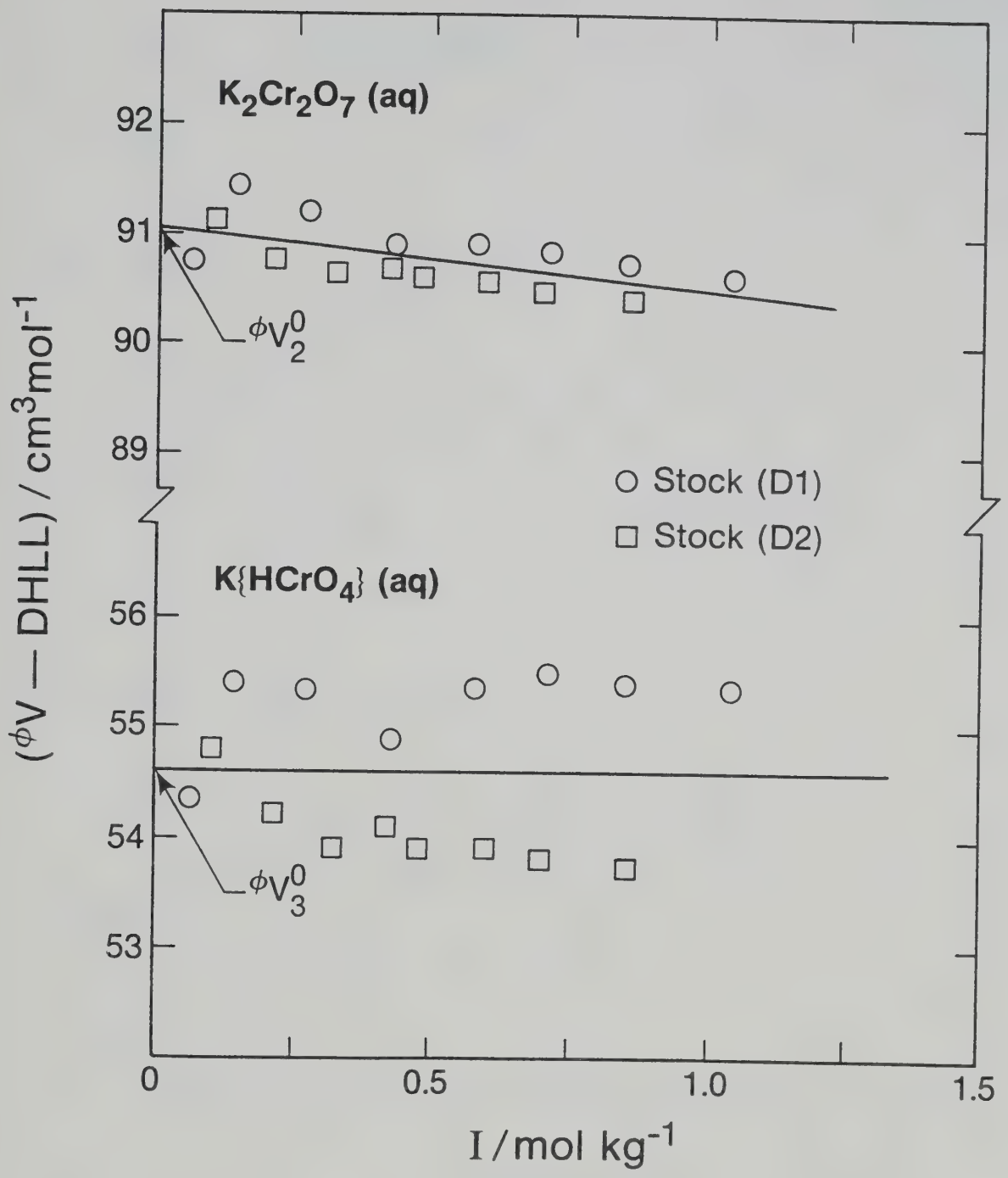

Figure 5.2: Experimental apparent molar volume data for aqueous solutions of $K_2Cr_2O_7$ plotted so that intercepts give ${}^{\phi}V^{\circ}$ values and slopes give B_V values.

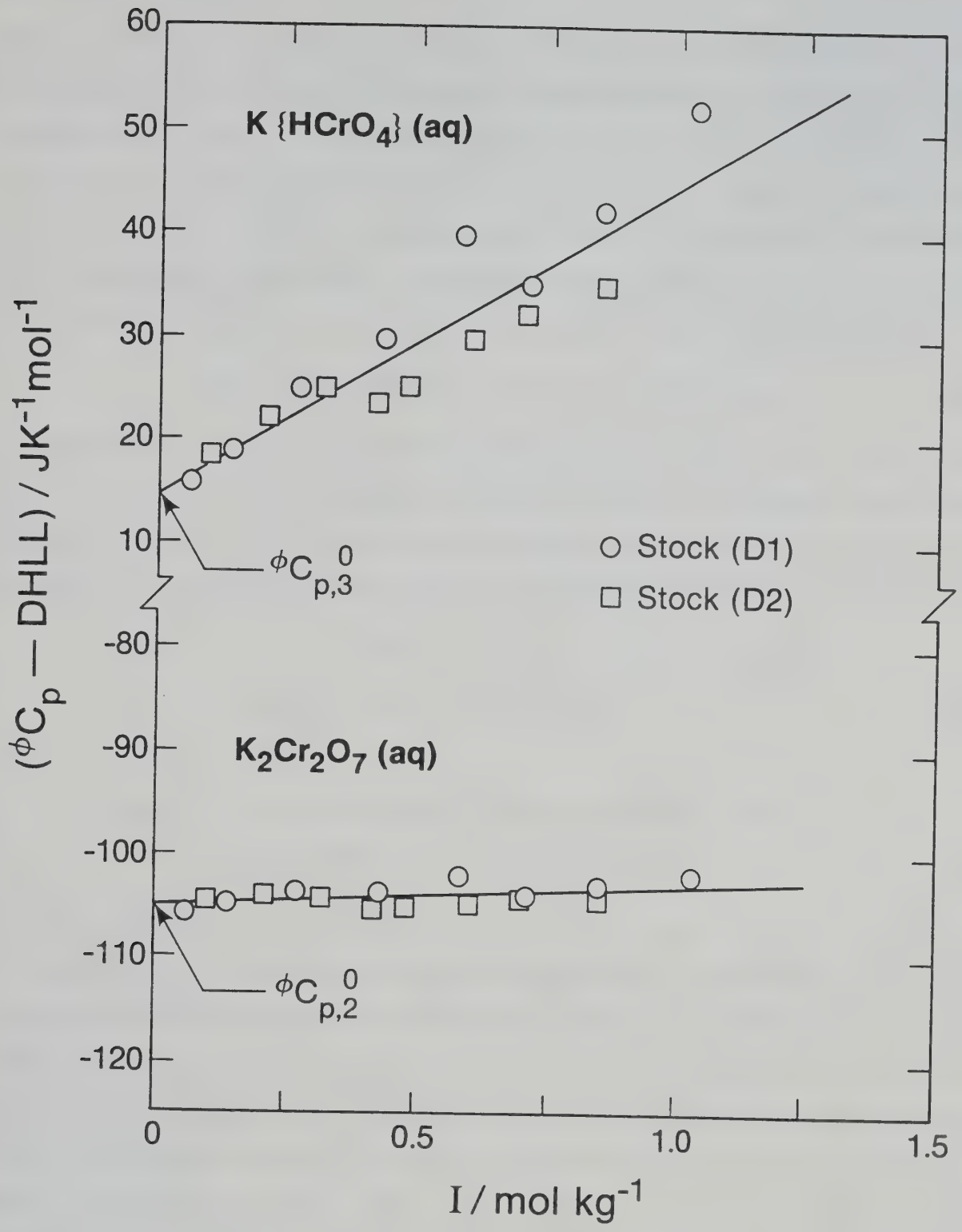

Figure 5.3: Experimental apparent molar heat capacity data for aqueous solutions of $K_2Cr_2O_7$ plotted so that intercepts give ${}^{\phi}C_p^{\circ}$ values and slopes give B_C values.

5.5.3 K_2CrO_4 (C2, C3)

Heat capacities and volumes of solutions of (K_2CrO_4 + KOH labelled C1) have been presented in a previous section, along with calculations based on these results. Allowing for the presence of very dilute KOH in these solutions presented a minor complication in deriving the desired standard state partial molar heat capacity and volume of aqueous K_2CrO_4. Consideration of the heat capacities of solutions of K_2CrO_4 dissolved in pure water, for which the complication in calculation is related to the reaction of chromate with water to form bichromate is represented by

$$CrO_4^{2-}(aq) + H_2O(l) = HCrO_4^-(aq) + OH^-(aq) \qquad (5.1)$$

The fraction of $CrO_4^{2-}(aq)$ ions that have reacted to form $HCrO_4^-(aq)$ is designated here by α. The relationships between the previously defined experimental quantities ${}^{\phi}V^{exp}$ and ${}^{\phi}C_p^{exp}$ and properties of single electrolytes that are shown below, are related to the apparent molar properties for the desired solute, K_2CrO_4, by:

$$\begin{aligned} {}^{\phi}V^{exp} &= (1-\alpha){}^{\phi}V(2K^+,\ CrO_4^{2-}) + \alpha{}^{\phi}V(K^+,\ HCrO_4^-) + \\ &\quad \alpha{}^{\phi}V(K^+,\ OH^-) - \alpha\bar{V}^{\circ}(H_2O) \end{aligned} \qquad (5.39)$$

$$\begin{aligned} {}^{\phi}C_p^{exp} &= (1-\alpha){}^{\phi}C_p(2K^+,\ CrO_4^{2-}) + \alpha{}^{\phi}C_p(K^+,\ HCrO_4^-) + \\ &\quad \alpha{}^{\phi}C_p(K^+,\ OH^-) - \alpha\bar{C}_p^{\circ}(H_2O) + {}^{\phi}C_p^{rel} \end{aligned} \qquad (5.40)$$

Expressions for the apparent molar volumes and heat capacities for (K^+, $HCrO_4^-$) were based on the properties previously discussed and summarized in Table 5.9. Properties for KOH solutions were taken from ROUX *et al.* (1984). The relaxation contributions to heat capacities, represented by ${}^{\phi}C_p^{rel}$, were calculated as previously described, with results listed in Table 5.7. Further calculations with equations of type 5.8 led to well-defined values for the limiting standard state volumes, heat capacities, and B_Y parameters for ($2K^+$, CrO_4^{2-}) that are listed in Table 5.9. Errors in these values due to uncertainties and possible errors in the properties of (K^+, $HCrO_4^-$) are less than the stated statistical uncertainties (standard deviations); the small effect of the properties of (K^+, $HCrO_4^-$) on the properties of ($2K^+$, CrO_4^{2-}) is due to the very small molalities of (K^+, $HCrO_4^-$) in all of these solutions. Graphs of the present results for these solutions (C2 and C3) are shown in Figure 5.1.

5.6 Discussion

5.6.1 Literature Comparisons

Millero's useful compilation (MILLERO, 1972) lists ${}^{\phi}V^{\circ}(K_2CrO_4, aq) = 37.12$ cm^3mol^{-1}, based on the measurements from JONES and COLVIN (1940). More recent measurements of OLOFSSON *et al.* (1978) have led to ${}^{\phi}V^{\circ} = 38.2$ cm^3mol^{-1} for this electrolyte. Still more recently, VASILEV *et al.* (1984) have reported ${}^{\phi}V^{\circ} = 37.43$ cm^3mol^{-1}; recalculations of this data using an equation of the form of eq. 5.8 has led to the revised value ${}^{\phi}V^{\circ} = 37.69 \pm 0.1$ cm^3mol^{-1}. The effects of hydrolysis of $CrO_4^{2-}(aq)$ as represented by eq. 5.1 are small and have been neglected in obtaining all of these values. Two of these values are in good agreement with ${}^{\phi}V^{\circ} = 37.91$, 38.15 and 37.64 cm^3mol^{-1} from the present measurements on solutions labelled C1, C2, and C3.

OLOFSSON *et al.* (1978) and VASILEV *et al.* (1984) have reported ${}^{\phi}C_p^{\circ} = -235.0$ and -244.7 $J\ K^{-1}mol^{-1}$, respectively, for (K_2CrO_4, aq). All of their reported heat capacities have been used in calculations of the type described here allowing for the presence of $(K^+, HCrO_4^-)$ and also contributions to the functions from chemical relaxation. Equations of type 5.8 were used along with the more modern values of A_Y that resulted in ${}^{\phi}C_p^{\circ} = -239.5 \pm 0.3$ $J\ K^{-1}mol^{-1}$ from the results of OLOFSSON *et al.* (1978) and ${}^{\phi}C_p^{\circ} = -233.2 \pm 1.7$ $J\ K^{-1}mol^{-1}$ from the results of VASILEV *et al.* (1984). It is seen that the present results of ${}^{\phi}C_p^{\circ} = -245.9$, -245.2 and -241.8 $J\ K^{-1}mol^{-1}$ for $(2K^+, CrO_4^{2-})$ from solutions labelled C1, C2, and C3, respectively, are in reasonable agreement with the earlier result from OLOFSSON *et al.* (1978), but in less good agreement with the recalculated ${}^{\phi}C_p^{\circ}$ from VASILEV *et al.* (1984). The heat capacities measured by VASILEV *et al.* (1984) were for more highly concentrated solutions than either the present results or those from OLOFSSON *et al.* (1978) and also appear to be less accurate.

Measurements by PESCE (1935) provided data that FAJANS and JOHNSON (1941) used to estimate the standard state volume of $Cr_2O_7^{2-}(aq)$. Because the measurements were on concentrated solutions and the presence of $HCrO_4^-(aq)$ and $CrO_4^{2-}(aq)$ was neglected in the calculations, the derived volume of $Cr_2O_7^{2-}(aq)$ is quite uncertain and contains substantial errors. More recent dilatometric titrations of solutions

of K_2CrO_4 with aqueous HCl by ROHWER *et al.* (1978) and their sensible data treatment have led them to reliable values as follows: ${}^{\phi}V^{\circ}(2K^+, Cr_2O_7^{2-}) = 87.81$ cm^3mol^{-1} and ${}^{\phi}V^{\circ}(K^+, HCrO_4^-) = 53.15$ cm^3mol^{-1}. Total uncertainties in these values appear to be slightly larger than the reported values of $\pm$ 0.9 and 0.18 cm^3mol^{-1}, respectively. The first of these volumes is in fair agreement with the present value ${}^{\phi}V^{\circ}(2K^+, Cr_2O_7^{2-}) = 91.1 \pm 0.3$ cm^3mol^{-1}, and the second value is in better agreement with the present ${}^{\phi}V^{\circ}(K^+, HCrO_4^-) = 54.6 \pm 0.5$ cm^3mol^{-1}, where these latter $\pm$ values are estimates of the total uncertainties in the presently derived standard state volumes.

No previously determined heat capacities of aqueous solutions containing dichromate were found to compare with the present results.

5.6.2 Selection of best values

Results of the measurements reported here on solutions made from K_2CrO_4 and $K_2Cr_2O_7$, in combination with previous results cited in the preceding section, permits evaluation of "best" conventional ionic partial molar volumes and heat capacities for CrO_4^{2-}(aq), $Cr_2O_7^{2-}$(aq) and $HCrO_4^-$(aq), all based on ${}^{\phi}Y^{\circ}(H^+, aq) \equiv 0$. Best values for the standard state partial molar heat capacities and volumes (equivalent to the limiting apparent molar properties) from weighted averages of all of the available data for K_2CrO_4 cited above are ${}^{\phi}V^{\circ}(K_2CrO_4, aq) = 38.0 \pm 0.3$ cm^3mol^{-1} and ${}^{\phi}C_p^{\circ}(K_2CrO_4, aq) = -245 \pm 3$ J $K^{-1}mol^{-1}$. These values, when combined with the conventional ionic volume and heat capacity for K^+(aq), lead to the conventional ionic properties for CrO_4^{2-}(aq) that are reported in Table 5.10. The value ${}^{\phi}V^{\circ}(K^+, aq) = 9.02$ cm^3mol^{-1} from MILLERO (1972), and ${}^{\phi}C_p^{\circ}(K^+, aq) = 12.8$ J $K^{-1}mol^{-1}$ from DESNOYERS *et al.* (1976) and ROUX *et al.* (1978) were used along with the selected properties for K_2CrO_4(aq) to obtain the conventional ${}^{\phi}V^{\circ}(CrO_4^{2-}, aq) = 19.9$ cm^3mol^{-1} and ${}^{\phi}C_p^{\circ}(CrO_4^{2-}, aq) = -271$ J $K^{-1}mol^{-1}$, as listed in Table 5.10. Similarly, combination of the present standard state properties for $K_2Cr_2O_7$ and K[$HCrO_4$] listed in Table 5.9 with properties for K^+(aq) cited above leads to the conventional ionic volumes and heat capacities of $Cr_2O_7^{2-}$(aq) and $HCrO_4^-$(aq) given in Table 5.10.

Table 5.10: Conventional [$^{\phi}Y^{\circ}(H^+, aq) \equiv 0$] ionic partial molar volumes and heat capacities for aqueous ions at 25° C, and properties for water.

Ion	$\bar{C}_p^{\circ}$ ($JK^{-1}mol^{-1}$)	$\bar{V}^{\circ}$ (cm^3mol^{-1})
H^+	0	0
K^+	12.8	9.03
OH^-	−140	−40.5
CrO_4^{2-}	−271	19.9
$Cr_2O_7^{2-}$	−131	73.0
$HCrO_4^-$	2	45.6
$H_2O(l)$	75.29	18.07

5.7 Equilibrium calculations

PALMER *et al.* (1987) have recently reported results of their potentiometric investigation of Cr(VI) hydrolysis in aqueous solutions of NaCl from 25 to 175°C. They have derived values for the standard state heat capacity changes associated with reactions represented by eq. 5.41 and 5.25

$$2CrO_4^{2-}(aq) + 2H^+(aq) = Cr_2O_7^{2-}(aq) + H_2O(l) \qquad (5.41)$$

and

$$CrO_4^{2-}(aq) + H^+(aq) = HCrO_4^-(aq) \qquad (5.25)$$

by double differentiation of their equilibrium constants according to eq. 5.4 and 5.5. These calculations have led to $\Delta C^\circ_{p,41} = 463 \pm 13$ J K^{-1}mol^{-1} and $\Delta C^\circ_{p,25} = 231 \pm 6$ J K^{-1}mol^{-1} at 25°C, where $\pm$ values are their statistical estimates of errors associated with their least squares fits. Calculations of these same heat capacity changes using the present calorimetric results listed in Table 5.10 lead to $\Delta C^\circ_{p,41} = 486 \pm 10$ J K^{-1}mol^{-1} and $\Delta C^\circ_{p,25} = 273 \pm 10$ J K^{-1}mol^{-1}, where these $\pm$ values are our estimates of *total* uncertainties in these quantities. The agreement here is amazingly good considering that the equilibrium data were differentiated twice to obtain their ΔC°_p values. This excellent agreement between the present calorimetrically measured values and the results of the equilibrium study, suggests strongly that the data of PALMER *et al.* (1987) accuratly describe the curvature in $\ln K$ versus $1/T$ van't Hoff plots.

It has been shown that ΔC°_p values for isocoulombic reactions (symmetric with respect to number and charge types of ions on both sides of a reaction equation), are small and reasonably independent of temperature over moderately wide ranges (LINDSAY, 1980; MURRAY and COBBLE, 1980; BARBERO *et al.*, 1982). It is then possible to use a ΔC°_p value for one temperature in integrating eqs. 5.4 and 5.5 to obtain calculated equilibrium constants that are expected to be quite accurate over reasonably wide ranges of temperature. It is also expected that ΔV° will be approximately independent of temperature and pressure, making it possible to use eq. 5.6 for similar calculations of $K = f(p)$.

The equilibrium reactions that are represented by eqs. 5.25 and 5.41 are not isocoulombic and hence not favourable for extrapolations of the type described above.

PALMER *et al.* (1987) have reported equilibrium constants for the related pseudo-isocoulombic reactions:

$$CrO_4^{2-}(aq) + H_2O(l) = HCrO_4^-(aq) + OH^-(aq) \qquad (5.1)$$

$$2CrO_4^{2-}(aq) + H_2O(l) = Cr_2O_7^{2-}(aq) + 2OH^-(aq) \qquad (5.19)$$

It is expected that the ΔC_p° values for these reactions are reasonably constant over moderate ranges of temperature even though the reactions are not rigorously isocoulombic. Combination and integration of eqs. 5.4, 5.5, and 5.6 for the special case of constant ΔC_p° and ΔV° values leads to

$$\ln K_{T,p} = \ln K_{298,1} + \frac{\Delta H^\circ}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right) + \frac{\Delta C_p^\circ}{R}\left[\ln\left(\frac{T}{298}\right) - 1 + \frac{298.15}{T}\right] - \frac{\Delta V^\circ}{RT}(p-1) \qquad (5.42)$$

Values for the equilibrium constants of the reactions represented by eqs. 5.1 and 5.19 have been calculated to high temperatures using pressures of 1 bar to 100°C and steam saturation pressures above (HAAR *et al.*, 1984). These calculated equilibrium constants are given along with the experimental values in Table 5.11. Good agreement is observed for temperatures up to 175°C for the reaction represented by eq. 5.19 and excellent agreement for the reaction represented by eq. 5.1. Figure 5.4 shows plots of the equilibrium constants from PALMER *et al.* (1987) and also equilibrium constants that have been calculated with eq. 5.42. These calculations clearly show that extrapolations of equilibrium constants for pseudo-isocoulombic reactions can provide accurate equilibrium constants (or standard state Gibbs free energy changes) to elevated temperatures. Further analysis of isocoulombic reactions in terms of high temperature equilibrium constant extrapolations are presented later in Chapters 14 through 16.

Table 5.11: Comparison of calculated (eq. 5.42) and experimental equilibrium constants for reactions involving Cr(VI) species.

	$2CrO_4^{2-} + H_2O = Cr_2O_7^{2-} + 2OH^-$			$CrO_4^{2-} + H_2O = HCrO_4^- + OH^-$	
t	log K			log K	
(°C)	Exp.*	Calc.†	Calc.‡	Exp.*	Calc.†
25	-13.30 ± 0.08	(-13.30)	(-13.30)	-7.44 ± 0.03	(-7.44)
75	-10.59 ± 0.08	-10.81	-10.55	-5.89 ± 0.02	-5.93
125	-8.55 ± 0.10	-8.88	-8.44	-4.73 ± 0.02	-4.74
175	-6.97 ± 0.13	-7.34	-6.75	-3.83 ± 0.03	-3.78

* These values are from PALMER *et al.* (1987)

† These values were calculated using the enthalpies listed in Table 5.6.

‡ These values were calculated using the enthalpy value for the reaction reported by PALMER *et al.*(1987).

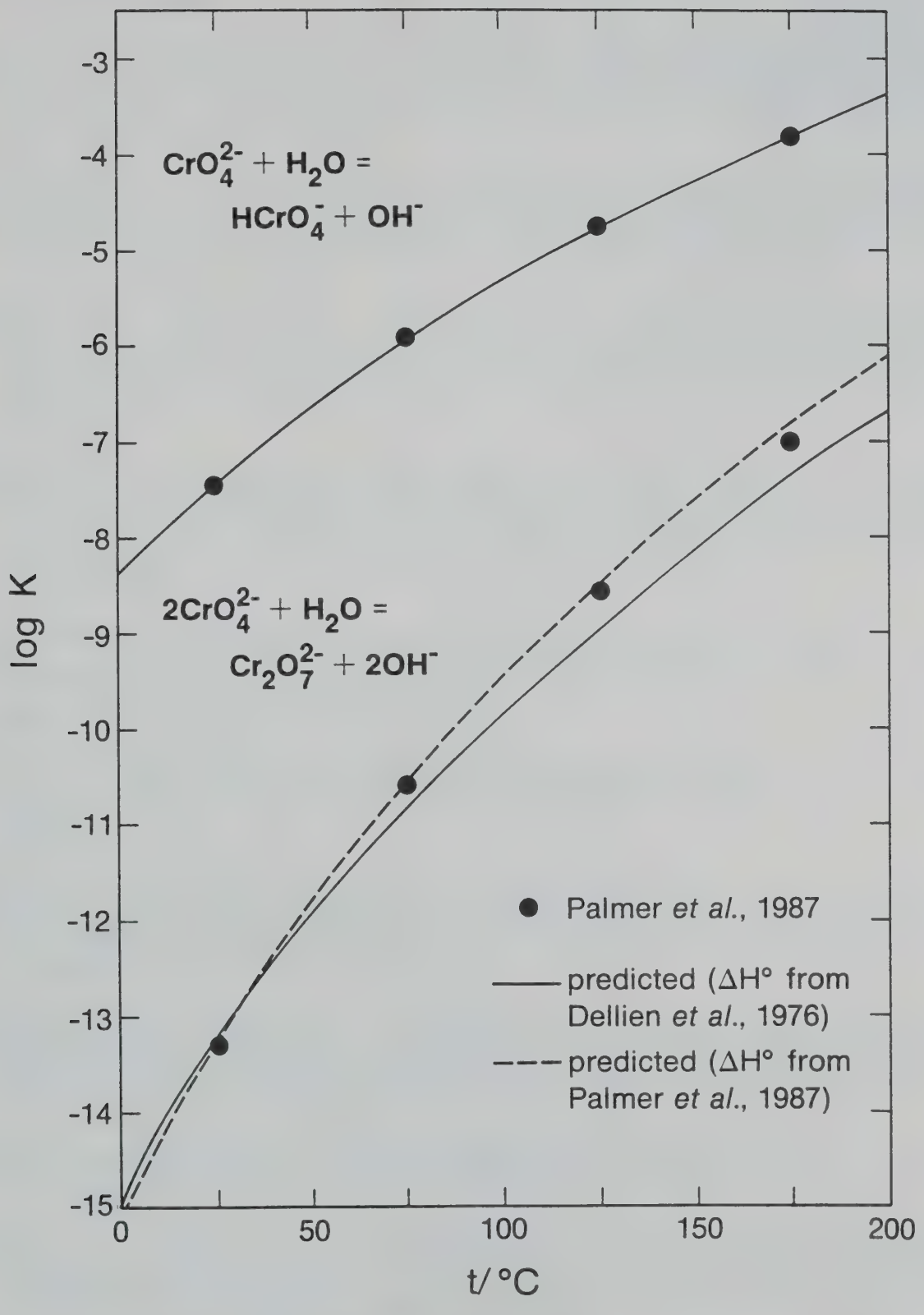

Figure 5.4: Comparison of equilibrium constants calculated with the present 25°C heat capacity measurements and direct experimental values for selected reactions involving chromate, bichromate, and dichromate aqueous ions.

5.8 References

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Chapter 6

Thermodynamics of aqueous aluminum: Standard partial molar heat capacities of Al^{3+}(aq) from 10 to 55°C[1]

6.1 Introduction

The thermodynamic properties of aqueous aluminum species are required for a variety of processes. For example, such data over wide ranges of temperature are required to model mineral dissolution and transport in steam injection and combustion processes for the *in situ* recovery of bitumen or heavy oil. The same data are needed to model aqueous solutions associated with the formation of hydrothermal ore deposits, geothermal power generation, the marine chemistry of deep hydrothermal vents, hydrometallurgy, and the corrosion behaviour of aluminum alloys. More recently, thermodynamic data for aqueous aluminum species are required to aid in the study of health-related problems (such as Alzheimer's disease) suspected of being caused by human intake of aluminum (MARTIN, 1986).

Equilibrium constants for the hydrolysis of Al^{3+}(aq) and some solubility data have been obtained up to 300°C (MESMER AND BAES, 1971; COUTURIER *et al.*, 1984; KUYUNKO, *et al.*, 1983; MARTYNOVA *et al.*, 1962 ; MACDONALD et al., 1973). There are limited data available for other aluminum complexes including mixed hydroxide - halide complexes over limited temperature ranges (SANJUAN *et al.*, 1987).

The Gibbs energy of formation of the aluminum ion, Al^{3+}(aq), is reasonably well established at 25°C (HEMINGWAY and ROBIE 1977). Values for the standard partial molar entropy and volume of Al^{3+}(aq) from different studies are much less

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consistent (HEMINGWAY and ROBIE 1977; MILLERO, 1972) and there is only one study of apparent molar heat capacities, at 25°C (BABAKULOV and LATYSHEVA, 1974). Entropy, heat capacity, and volume data are important in the development of comprehensive equations of state that can describe standard state properties of aqueous ions over wide ranges of temperature and pressure (PITZER *et al.*, 1984; HELGESON *et al.*, 1981; HOLMES and MESMER, 1983; TREMAINE *et al.* , 1986). One purpose of this work has been to obtain the standard state partial molar heat capacity for Al^{3+}(aq) from 10 to 55°C by measuring apparent molar heat capacities of aqueous solutions containing the chloride and nitrate salts. Apparent molar volumes were also measured for all of these solutions at 25°C. A more detailed analysis of the apparent molar volumes of aqueous solutions containing Al^{3+}(aq) can be found in BARTA and HEPLER (1986).

6.2 Experimental

Water used in all of the experiments was first distilled and then passed through a Milli-RO4/Milli-Q reagent grade mixed bed ion exchange and activated carbon system (final resistivity of 18 MΩ cm or greater). Fisher certified ACS $Al(NO_3)_3 \cdot 9H_20$ was recrystallized twice from 0.02 m HNO_3 by cooling the solution slowly from 50°C to room temperature and then to 0°C. $AlCl_3 \cdot 6H_2O$ from Alfa (Puratonic, "certified 99.999 percent") was used without further purification.

To suppress hydrolysis, the aluminum stock solutions were prepared by dissolving the nitrate and chloride salts in standard solutions of dilute HNO_3 and HCl, respectively. The nitrate stock solution showed that significant amounts of residual acid was on the crystals. The total nitric acid molality was therefore determined by careful measurements of the pH of the stock solution, using a calibrated glass electrode. The molality of hydrochloric acid in the chloride stock solution was determined by calculation (based on analytical determination of Al^{3+} and known amounts of added HCl) and confirmed by pH measurements. The stock solutions were analyzed gravimetrically for aluminum by homogenous precipitation with 8-hydroxyquinoline (VOGEL, 1978). The compositions of the stock solutions are listed in Table 6.1. More dilute solutions were prepared by weight from the stock solutions using standardized

10^{-3} m HNO_3 or HCl as diluent.

The heat capacities and densities of all solutions were measured relative to water with a Sodev CP-C flow microcalorimeter (PICKER *et al.*, 1971) and 03D densimeter (PICKER *et al.*, 1974). Water and a standard solution of 1.0 m NaCl were used to calibrate the densimeter. Temperatures from 10 to 55°C were maintained to ± 0.001 °C in the calorimeter by a Sodev CT-L temperature bath and monitored by thermistors calibrated with an HP 2804A quartz thermometer traceable to NBS standards.

The densimeter and calorimeter delay line were both thermostated to 25.000 ± 0.005 °C using a second Sodev CT-L bath. In this configuration the differential calorimetric signal that was discussed in Chapter 2 is a heat capacity-density ratio of the form $\left(\frac{c_p d_{298}}{c_{p,w} d_{w,298}} - 1\right)$. Here, c_p and $c_{p,w}$ are the specific heats of the solution and pure water at the temperature of the calorimeter, and d_{298} and $d_{w,298}$ are the corresponding densities at the temperature of the delay line, 25.00°C. The need for (less accurate) high temperature densities is thereby eliminated (SMITH-MAGOWAN and WOOD, 1981 ; TREMAINE *et al.*, 1986). Densities and specific heat capacities for water were taken from KELL'S compilations (1967, 1972): $d_{w,298}$ = 0.997047 g cm^{-3}, and $c_{p,w}$ = 4.1919, 4.1793, 4.1783 and 4.1821 J $K^{-1}g^{-1}$ at 10, 25, 40, and 55°C respectively.

The experimental values of $\left(\frac{c_p d_{298}}{c_{p,w} d_{w,298}} - 1\right)$ were corrected for a small heat leak. The correction factor was obtained daily at 25°C by calibration with a standard solution of 1m NaCl (DESNOYERS *et al.* , 1976; WHITE and WOOD, 1982) and was assumed to be independent of temperature. The factor f fluctuated between 1.002 and 1.007.

6.3 Results

6.3.1 Apparent Molar Properties

Aqueous Al^{3+} can form mononuclear and dinuclear hydrolysis products, according to the reactions (BOTTERO *et al.*, 1980; BAES and MESMER, 1976)

$$Al^{3+}(aq) + OH^{-}(aq) = AlOH^{2+}(aq) \qquad (6.1)$$

$$2Al^{3+}(aq) + 2OH^{-}(aq) = Al_2(OH)_2^{4+}(aq) \qquad (6.2)$$

Calculations based on critically evaluated hydrolysis constant data (BAES and MESMER, 1976) indicate that the relative concentration of each hydrolyzed ion should be much less than 1 per cent of total aluminum in the solutions studied here. The following analysis is based on the premise that the solutions contained two stoichiometric solutes, HX and AlX_3 (X = Cl^- or NO_3^-) of known molalities, m, and that no significant hydrolysis takes place.

The experimental apparent molar heat capacity, ${}^{\phi}C_p^{exp}$, or volume, ${}^{\phi}V^{exp}$, is defined by the expression

$${}^{\phi}Y^{exp} = \frac{Y_{soln} - 55.509Y_w^{\circ}}{m_{AlX_3} + m_{HX}} \qquad (6.3)$$

where Y_w° is the molar heat capacity or volume of pure water. Values of ${}^{\phi}C_p^{exp}$ and ${}^{\phi}V^{exp}$ are listed in Table 6.1, along with the experimental data.

The contribution of each electrolyte in the mixture can be described by Young's rule (YOUNG and SMITH, 1954; REILLY and WOOD, 1969).

$${}^{\phi}Y^{exp} = \frac{m_{AlX_3}}{m_{AlX_3} + m_{HX}} {}^{\phi}Y(AlX_3,\ aq) + \frac{m_{HX}}{m_{AlX_3} + m_{HX}} {}^{\phi}Y(HX,\ aq) + \delta \qquad (6.4)$$

Here, ${}^{\phi}Y(AlX_3,\ aq)$ and ${}^{\phi}Y(HX,\ aq)$ are the values for the hypothetical solution of the pure components with speciation and ionic strength identical to the mixture, and δ is an excess mixing term. Because the concentration of acid (HX) was sufficiently small in relation to that of aluminum so that the contributions of acid were almost negligible, δ may be ignored without affecting the following calculations. Rearrangement of eq. 6.4 leads to

$${}^{\phi}Y(AlX_3,\ aq) = \frac{m_{AlX_3} + m_{HX}}{m_{AlX_3}} {}^{\phi}Y^{exp} - \frac{m_{HX}}{m_{AlX_3}} {}^{\phi}Y(HX,\ aq) \qquad (6.5)$$

Values of ${}^{\phi}V(HCl,\ aq)$ at 25°C and ${}^{\phi}C_p$ (HCl, aq) from 10 to 55°C were obtained from TREMAINE *et al.* (1986). Values for ${}^{\phi}V(HNO_3,\ aq)$ and ${}^{\phi}C_p$ (HNO_3, aq) were taken from measurements of ENEA *et al.* (1977). The estimated (by Young's rule) contribution that HNO_3 makes to the apparent molar properties in these solutions may be in error at the higher ionic strengths. The effect on ${}^{\phi}Y(AlX_3,\ aq)$ is small, and must decrease to zero in extrapolations to infinite dilution. The values of ${}^{\phi}C_p$ and ${}^{\phi}V$ for $AlCl_3$(aq) and $Al(NO_3)_3$(aq) from eq. 6.5 are given in Tables 6.1 and 6.2.

Table 6.1: Experimental apparent molar volumes and heat capacities for aqueous $AlCl_3$ and $Al(NO_3)_3$ at 25°C.

m_{AlCl_3} (mol kg^{-1})	m_{HX} (mol kg^{-1})	$d_{298} - d_{w,298}$ (g cm^{-3})	ϕV^{exp} (cm^{3}mol^{-1})	$\frac{m_{HX}}{m_{AlX_3}}\phi V(HX)$ (cm^{3}mol^{-1})	$\phi V(AlX_3)$ (cm^{3}mol^{-1})	$\left(\frac{c_p d_{298}}{c_{p,w} d_{w,298}} - 1\right)$	ϕC_p^{exp} (J K^{-1}mol^{-1})	$\frac{m_{HX}}{m_{AlX_3}}\phi C_p(HX)$ (J K^{-1}mol^{-1})	$\phi C_p(AlX_3)$ (J K^{-1}mol^{-1})
				$AlCl_3$					
0.4667	0.01673	0.052914	19.24	0.68	19.25	−0.04867	−347.3	−3.9	−355.9
0.3179	0.01172	0.036591	17.97	0.70	17.93	−0.03411	−363.0	−4.1	−372.3
0.1782	0.00701	0.020861	16.44	0.74	16.34	−0.01995	−386.0	−4.5	−396.7
0.1389	0.00568	0.016350	15.86	0.77	15.74	−0.01575	−393.4	−4.8	−404.7
0.1076	0.00463	0.012739	15.34	0.81	15.19	−0.01209	−390.1	−5.0	−402.0
0.07874	0.00366	0.009396	14.57	0.87	14.38	−0.009138	−406.4	−5.5	−419.7
0.05083	0.00272	0.006134	13.47	0.99	13.20	−0.005969	−413.2	−6.4	−428.9
0.03261	0.00210	0.003958	13.08	1.19	12.73	−0.003877	−415.7	−7.8	−434.6
				$Al(NO_3)_3$					
0.4446	0.00686	0.070138	51.43	0.38	51.84	−0.03974	−164.6	1.5	−168.7
0.2924	0.00485	0.046748	50.61	0.44	51.01	−0.02811	−192.9	0.8	−196.9
0.1903	0.00351	0.030729	49.88	0.52	50.28	−0.01930	−215.1	0.2	−219.3
0.1394	0.00284	0.022673	49.18	0.59	49.60	−0.01454	−227.9	−0.1	−232.4
0.1134	0.00250	0.018508	48.87	0.64	49.31	−0.01175	−225.2	−0.4	−229.8
0.09067	0.00220	0.014935	47.59	0.71	48.03	−0.009691	−242.6	−0.6	−247.9
0.05163	0.00168	0.008549	47.15	0.97	47.72	−0.005687	−253.5	−1.4	−260.4
0.04245	0.00156	0.007066	46.44	1.10	47.05	−0.004704	−257.1	−1.7	−264.8

Table 6.2: Experimental apparent molar heat capacities of $AlCl_3$ at 10, 40, and 55°C.

m_{AlCl_3} (mol kg^{-1})	m_{HCl} (mol kg^{-1})	$\left(\frac{c_p d_{298}}{c_{p,w} d_{w,298}} - 1\right)$	${}^{\phi}C_p^{exp}$ (J K^{-1}mol^{-1})	$\frac{m_{HCl}}{m_{AlCl_3}} {}^{\phi}C_p(HCl)$ (J K^{-1}mol^{-1})	${}^{\phi}C_p(AlCl_3)$ (J K^{-1}mol^{-1})
		10.00°C			
0.4667	0.0167	−0.05698	−421.6	−3.8	−432.9
0.4667	0.0167	−0.05703	−422.0	−3.8	−433.3
0.3179	0.0117	−0.03659	−443.4	−4.3	−455.4
0.1782	0.00701	−0.02331	−463.9	−5.0	−477.1
0.1389	0.00568	−0.01864	−479.0	−5.4	−493.3
0.1076	0.00463	−0.01460	−485.8	−5.8	−501.0
0.07874	0.00366	−0.01065	−484.9	−6.3	−501.1
		40.00°C			
0.4667	0.0167	−0.04366	−300.7	−3.6	−310.5
0.3179	0.0117	−0.03063	−315.7	−3.8	−326.3
0.1782	0.00701	−0.01780	−334.3	−4.1	−346.1
0.1389	0.00568	−0.01394	−337.8	−4.3	−350.1
0.1076	0.00463	−0.01101	−346.7	−4.6	−360.1
0.07874	0.00366	−0.008117	−351.4	−5.0	−365.6
0.05083	0.00272	−0.005413	−366.6	−5.8	−383.3
0.03261	0.00210	−0.003626	−382.3	−7.1	−402.8
		55.00°C			
0.4667	0.0167	−0.04041	−274.9	−3.4	−281.4
0.3179	0.0117	−0.02901	−297.8	−3.6	−305.2
0.1782	0.00701	−0.01687	−316.0	−3.9	−324.5
0.1389	0.00568	−0.01311	−315.7	−4.1	−324.5
0.1076	0.00463	−0.01036	−325.4	−4.4	−335.2
0.07874	0.00366	−0.007835	−340.0	−4.8	−351.0
0.05083	0.00272	−0.004939	−332.4	−5.5	−344.6
0.03261	0.00210	−0.003237	−338.3	−6.8	−353.3

6.3.2 Data Representation

Several approaches for the use of extended Debye-Hückel equations have been developed in recent years to describe the molality dependence of apparent molar properties over wide ranges of temperature (PITZER *et al.*, 1984; HELGESON *et al.*, 1981; HOLMES and MESMER, 1983; MILLERO, 1979). The data in Tables 6.1 and 6.2 are well represented by the expressions (MILLERO, 1979; PITZER and BREWER, 1961).

$$^{\phi}C_p = {}^{\phi}C_p^{\circ} + \omega A_J(\frac{3}{2})\left(\frac{1}{\Lambda} - \frac{\sigma}{3}\right) I^{1/2} + B_Y I + C_Y I^{3/2} \tag{6.6}$$

$$^{\phi}V = {}^{\phi}V^{\circ} + \omega A_V(\frac{3}{2})\left(\frac{1}{\Lambda} - \frac{\sigma}{3}\right) I^{1/2} + B_Y I + C_Y I^{3/2} \tag{6.7}$$

A_J and A_V are the Debye-Hückel limiting slopes for apparent molar properties, and were taken from BRADLEY and PITZER'S equation (1979) as reported by ANANTHASWAMY and ATKINSON (1984). The ionic strength, I, and other terms in eqs. 6.6 and 6.7 are defined as follows.

$$I = \omega m = \frac{1}{2}\sum m_i z_i^2 \tag{6.8}$$

$$\Lambda = 1 + I^{1/2} \tag{6.9}$$

$$\sigma = \frac{3\left(\Lambda - \frac{1}{\Lambda} - 2\ln\Lambda\right)}{I^{3/2}} \tag{6.10}$$

Equations of the type described by eqs. 6.6 and 6.7 were fitted to all of the data for AlX_3(aq) in Tables 6.1 and 6.2. Data for solutions with molalities below 0.07 were regarded as suspect and were assigned a statistical weighting of 10 per cent relative to data obtained at higher molalities. Further, the data for $^{\phi}C_p$ ($AlCl_3$, aq) could be represented, with an increase in the overall variance of only three per cent, by using the following expressions to describe the temperature dependence of B_J and C_J in terms of temperature in kelvins:

$$B_J = a_1 + a_2 T \tag{6.11}$$

$$C_J = a_3 + a_4 T + a_5 T^2 \tag{6.12}$$

Values for all the parameters obtained from this fitting procedure are listed in Tables 6.3 and 6.4. The values for $^{\phi}C_p$ and $^{\phi}V$ from the above calculation procedure are

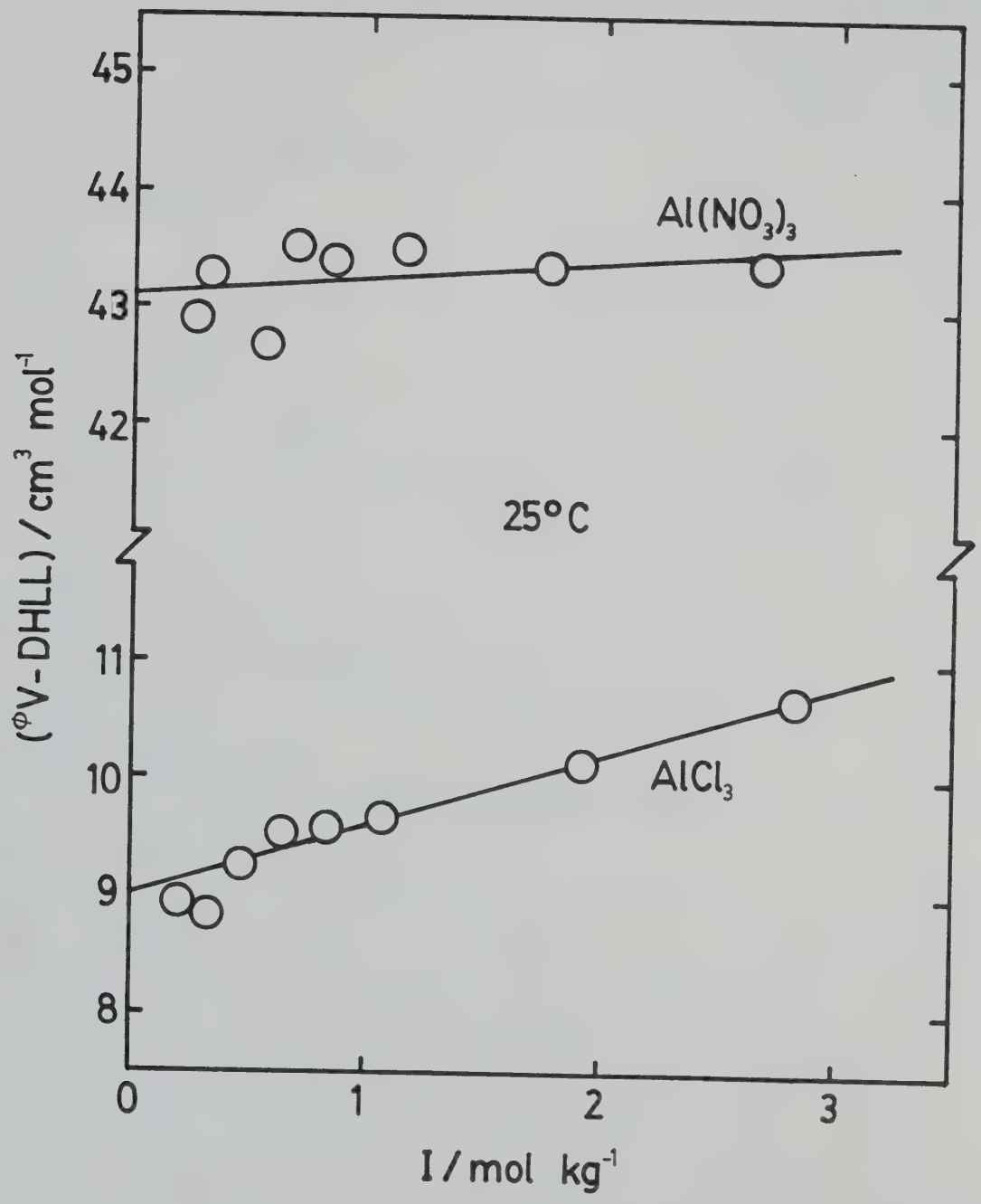

Figure 6.1: The apparent molar volumes of $Al(NO_3)_3(aq)$ and $AlCl_3(aq)$, plotted against ionic strength after subtracting the Debye-Hückel limiting law (DHLL) term according to eq. 6.7. The least squares fits are shown as solid curves.

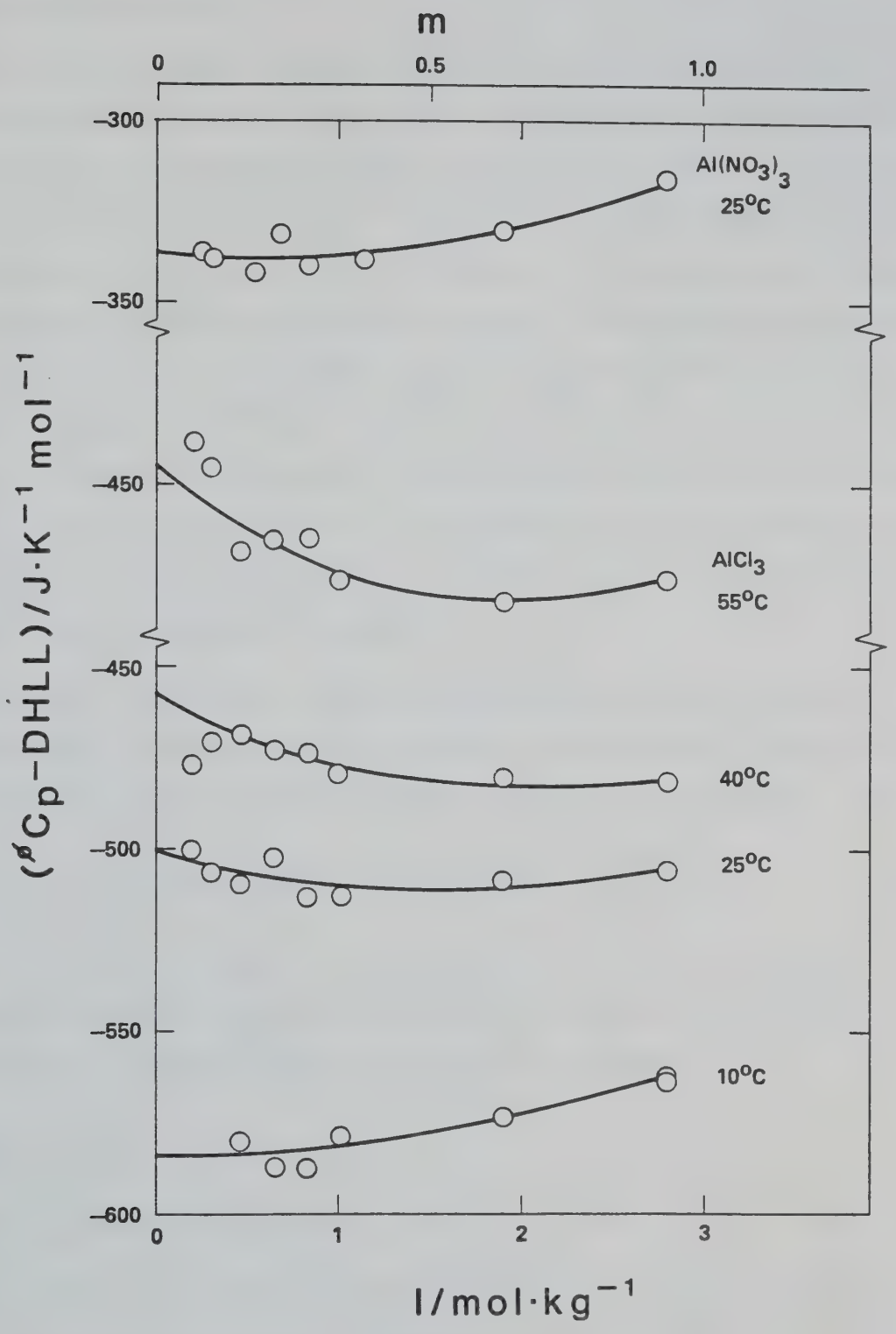

Figure 6.2: The apparent molar heat capacities of $Al(NO_3)_3(aq)$ and $AlCl_3(aq)$, plotted against ionic strength after subtracting the Debye-Hückel limiting law (DHLL) term according to eq. 6.6. The least squares fits are shown as solid curves.

plotted in Figures 6.1 and 6.2 after subtraction of the Debye-Hückel limiting law given by eqs. 6.6 through 6.10.

Because the ionic strengths are larger than the molalities approximately by the factor ω=6, these measurements extend only to *moderately* low ionic strengths. Furthermore, the Debye-Hückel limiting slopes, ωA_Y, are steep relative to those for 1:1 electrolytes. As a result, the values of ${}^{\phi}C_p^{\circ}$ and ${}^{\phi}V^{\circ}$ obtained by extrapolation to zero ionic strength are sensitive to the values chosen for A_J and A_V, and to the form of the extended Debye-Hückel equation that is used. The standard deviations from the fits in which the B and C parameters were not constrained to eqs. of type 6.11 and 6.12 were less than 0.8 cm^3 mol^{-1} for ${}^{\phi}V^{\circ}$, 2 J $K^{-1}mol^{-1}$ for ${}^{\phi}C_p^{\circ}$ at 25, 40 and 55°C, and 8 J $K^{-1}mol^{-1}$ for ${}^{\phi}C_p^{\circ}$ at 10°C. The sensitivity of both properties to values of A_V and A_J from different compilations, and to different fitting equations, leads us to assign overall uncertainty limits of $\pm$ 1 cm^3 mol^{-1} and $\pm$ 10 J $K^{-1}mol^{-1}$ to ${}^{\phi}V^{\circ}$ and ${}^{\phi}C_p^{\circ}$ values that are listed in Table 6.3.

The temperature dependent values of ${}^{\phi}C_p^{\circ}$ ($AlCl_3$, aq) can be represented to within 0.4 J $K^{-1}mol^{-1}$ by an equation of the type used to represent data for HCl(aq) (TREMAINE *et al.*, 1986) and the alkali halides (HOLMES and MESMER, 1983):

$$ {}^{\phi}C_p(AlCl_3,\ aq) = 2312.8 - 5.853T - \frac{115406}{T - 190} \qquad (6.13) $$

The term $1/(T - 190)$ describes the steep rise in ${}^{\phi}C_p^{\circ}$ from very negative values approaching 0°C and was chosen to be identical to that used for aqueous HCl (TREMAINE *et al.*, 1986) for convenience in later calculations.

6.4 Discussion

6.4.1 Standard State Properties

The values for ${}^{\phi}C_p^{\circ}$ and ${}^{\phi}V^{\circ}$ presented above are, by definition, identical to the standard partial molar heat capacity, $\bar{C}_p^{\circ}$, and volume $\bar{V}^{\circ}$. Al^{3+}(aq) is thought to be so strongly hydrated that it does not form ion pairs with the chloride ion (FRATIELLO *et al.*, 1968) or oxyanions such as SO_4^{2-}(aq) (AKITT and FARNSWORTH, 1985; LO *et al.*, 1982) and NO_3^-(aq) (FRATIELLO *et al.*, 1968; BOL and WELZEN, 1977) at ionic strengths below about 2 m. It is therefore assumed that the values for $\bar{C}_p^{\circ}(AlX_3,\ aq)$

Table 6.3: Standard state partial molar volumes, heat capacities, and ionic strength parameters.*

		volumes		
solute	t (°C)	${}^{\phi}V^{\circ}$ ($cm^3 mol^{-1}$)	B_V ($cm^3 kg\ mol^{-2}$)	C_V ($cm^3 kg^{3/2} mol^{-5/2}$)
$Al(NO_3)_3$	25	43.1	0.1392	0
$AlCl_3$	25	9.0	0.5995	0

		heat capacities		
solute	t (°C)	${}^{\phi}C_p^{\circ}$ (J $K^{-1} mol^{-1}$)	B_J (J kg $K^{-1} mol^{-2}$)	C_J (J $kg^{3/2} K^{-1} mol^{-5/2}$)
$Al(NO_3)_3$	25	−335.3	−16.37	14.27
†$AlCl_3$	10	−583.3	−7.867	9.023
	25	−499.3	−24.34	13.15
	40	−456.9	−40.82	19.51
	55	−443.2	−57.29	26.89

* $A_V = 1.8743\ cm^3 kg^{1/2} mol^{-3/2}$ at 25 °C.

$A_J = 28.446, 32.783, 37.446, 42.699\ J\ K^{-1} kg^{1/2} mol^{-3/2}$ at 10, 25, 40, and 55 °C.

† $B_J = 303.131 - 1.09835\ T$

$C_J = 246.073 - 1.90473\ T + 0.00376989\ T^2$

and $\bar{V}°(AlX_3, aq)$ obtained here correspond to standard state solutions containing only $Al^{3+}(aq)$ and $Cl^-(aq)$ or $NO_3^-(aq)$. Conventional standard state properties for $Cl^-(aq)$ and $NO_3^-(aq)$ are listed in Table 6.4. Combining these with the values for ${}^{\phi}V°$ from Table 6.3 yields the values $\bar{V}°(Al^{3+}, aq) = -45.3$ cm^3 mol^{-1} and -45.4 cm^3 mol^{-1}, respectively. The values for ${}^{\phi}C_p^{\circ}$ both give $\bar{C}_p^{\circ}(Al^{3+},aq)$ = -119 J K^{-1}mol^{-1}. The amazingly excellent agreement between results from both salts strongly supports the assumption that ion pairing has no significant effect. Averaged "best" values are listed in Table 6.4.

The temperature dependence of $\bar{C}_p^{\circ}(Cl^-, aq)$ is the same as that for $\bar{C}_p^{\circ}(HCl, aq)$ on the conventional ionic scale $[\bar{Y}°(H^+, aq) \equiv 0]$. From TREMAINE *et al.*, (1986),

$$\bar{C}_p^{\circ}(HCl, aq) = 582.2 - 1.467T - \frac{29356}{T - 190} \qquad (6.14)$$

where T is the absolute temperature (K). Combining eqs. 6.13 and 6.14 yields the following expression that is valid in the temperature range 10 to 55°C:

$$\bar{C}_p^{\circ}(Al^{3+}, aq) = 566.2 - 1.452T - \frac{27338}{T - 190} \qquad (6.15)$$

There are few other studies to compare with these results. COUTURE and LAIDLER (1956) obtained the values ${}^{\phi}V°(AlCl_3, aq) = 12.9$ cm^3 mol^{-1} and ${}^{\phi}V°[Al(NO_3)_3, aq] = 43.0$ cm^3 mol^{-1}, while FAJANS and JOHNSON (1942) reported ${}^{\phi}V°$ $(AlCl_3, aq) = 11.1$ cm^3 mol^{-1}. The nitrate result is in excellent agreement with the presently reported values. Both earlier measurements on the chloride are too positive by about 2 cm^3 mol^{-1} for consistency with our result for $Al^{3+}(aq)$. AKITT and FARNSWORTH (1985) have reported data for $Al_2(SO_4)_3(aq)$ that lead to the value $\bar{V}°(Al^{3+}, aq)$ = -39 cm^3 mol^{-1}. This result has a large uncertainty due to the steep Debye-Hückel slope ($\omega = 15$) and to ion-pairing effects at ionic strengths above about 2 molal.

BABAKULOV and LATYSHEVA (1974) have measured ${}^{\phi}C_p[Al(ClO_4)_3, aq]$ at 25°C from 0.1 to 3 m (I = 0.6 to 18 m). A least squares fit of equation (6.6) to their data ($I \leq 9m$) yields ${}^{\phi}C_p[Al(ClO_4)_3, aq] = -214 \pm 8$ J K^{-1}mol^{-1}. From ${}^{\phi}C_p^{\circ}(ClO_4^-, aq)$ = -25 J K^{-1}mol^{-1} (ROUX *et al.*, 1978), the value $\bar{C}_p^{\circ}(Al^{3+}, aq) = -133$ J K^{-1}mol^{-1} can be calculated, that is in fair agreement with the present value of -119 J K^{-1}mol^{-1} from Table 6.4. Because these measurements extend to lower molalities and yielded identical values for $\bar{C}_p^{\circ}$ from two different salts, we believe them to be the more accurate.

Table 6.4: Standard state properties of selected aqueous species at 25°C.

ion	$\bar{V}^\circ$ ($cm^3 mol^{-1}$)	$\bar{C}_p^\circ$ ($J\ K^{-1} mol^{-1}$)
$H^+(aq)$	0	0
$Cl^-(aq)$	18.1	−126.6
$NO_3^-(aq)$	29.5	−72.1
$Al^{3+}(aq)$	−45.3	−119.3

6.4.2 Correlations at 25°C

Because of its high charge, Al^{3+}(aq) provides a severe test for correlations that attempt to predict standard partial molar properties. SWADDLE and MAK (1983) have reported an equation that relates $\bar{V}°(M^{z+}, aq)$ to ionic radius, charge and hydration number. The value calculated from the Swaddle-Mak equation, $\bar{V}°(Al^{3+},aq)$ = –42.1 cm^3 mol^{-1}, is in reasonable agreement with our experimental value, –45.3 cm^3 mol^{-1}.

The most widely used predictive scheme for the estimation of the heat capacities of aqueous ions is the semi-empirical entropy correspondence principle (CRISS and COBBLE, 1964a,b). For cations, $\bar{C}_p°(M^{z+}, aq)$ can be calculated from the standard state entropy at 25°C, according to the equation

$$\bar{C}_p°(M^{z+},\ aq)/(J\ K^{-1}mol^{-1}) = 174.05 - 0.523(\bar{S}° - 20.9z) - z(117.2) \qquad (6.16)$$

The value $\bar{S}°(Al^{3+},\ aq)$ = –308 ± 15 J $K^{-1}mol^{-1}$ from HEMINGWAY and ROBIE (1977) yields the Criss-Cobble prediction $\bar{C}_p°(Al^{3+},aq)$ = 16 J $K^{-1}mol^{-1}$, in poor agreement with the experimental value –119 J $K^{-1}mol^{-1}$. MORSS and MCCUE (1976) reported much better agreement with the Criss-Cobble equation for $\bar{C}_p°(Th^{4+},\ aq)$. The failure of the correspondence principle for Al^{3+}(aq) suggests that its success with the more highly charged Th^{4+}(aq) ion may well be fortuitous.

6.4.3 Extrapolations to Elevated Temperatures

HELGESON, KIRKHAM, and FLOWERS (1981) (HKF) have developed equations to describe the dependence of $\bar{C}_p°$ and $\bar{V}°$ on temperatures and pressures. This treatment is based on the assumption that at high temperatures both properties can be described using the simple Born equation for a charged sphere in a dielectric continuum. For heat capacities at constant pressure, the HKF equation is:

$$\bar{C}_p° = c_1 + \frac{c_2 T}{T - \theta} + \omega T X \qquad (6.17)$$

Here, the terms c_1, c_2 and θ are adjustable parameters that describe the steep rise in $\bar{C}_p°$ just above 0°C. The term ωTX results from the Born equation for $\bar{C}_p°$ (as

discussed in detail in Chapter 18), where

$$X = \frac{1}{\epsilon}\left[\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_p - \left(\frac{\partial \ln \epsilon}{\partial T}\right)_p^2\right] \tag{6.18}$$

$$\omega/(\text{J mol}^{-1}) = 6.9466 \times 10^5 \frac{z^2}{r}\text{Å} \tag{6.19}$$

Here, ϵ is the static dielectric constant of water as tabulated by HELGESON and KIRKHAM (1974), and r is an effective electrostatic radius of the ion (HELGESON *et al.*, 1981), that yields $\omega = 30.29$ J mol^{-1} for $AlCl_3$(aq), using crystallographic radii from SHANNON (1976). The premise behind eq. 6.17 is that even approximate models for the high temperature behavior of $\bar{C}_p^\circ$ yield accurate extrapolations of Gibbs energies if the low temperature heat capacity function is accurately known. Confirmation of this idea was shown in Chapter 4, using recent data for aqueous HCl (TREMAINE *et al.*, 1986).

The HKF model fits the results for $\bar{C}_p^\circ(AlCl_3, \text{aq})$ in Table 6.3 with a maximum deviation of less than 2 J K^{-1}mol^{-1}, using the value $\theta = 246$ which was obtained from an earlier study on HCl(aq) (TREMAINE *et al.*, 1986). Results of these calculations can be summarized by

$$\bar{C}_p^\circ(AlCl_3,\ \text{aq}) = 113.2 - \frac{56.91T}{T - 246} + 30.29 \times 10^5 TX \tag{6.20}$$

and from TREMAINE *et al.* (1986)

$$\bar{C}_p^\circ(HCl,\ \text{aq}) = 14.2 - \frac{14.52T}{T - 246} + 6.093 \times 10^5 TX \tag{6.21}$$

Therefore

$$\bar{C}_p^\circ(Al^{3+},\ \text{aq}) = 70.6 - \frac{13.36T}{T - 246} + 12.01 \times 10^5 TX \tag{6.22}$$

A graph based on equation 6.20 is plotted in Figure 6.3, along with the direct experimental results and the Born function, ωTX. The data approach Born behaviour at elevated temperatures and are consistent with the HKF model, except for small differences in the Debye-Hückel limiting slopes used here and those generated by HELGESON *et al.* (1981). It is suggested that eqs. 6.20 and 6.22 be used as provisional heat capacity functions for high temperature calculations until data from direct measurements at higher temperatures become available.

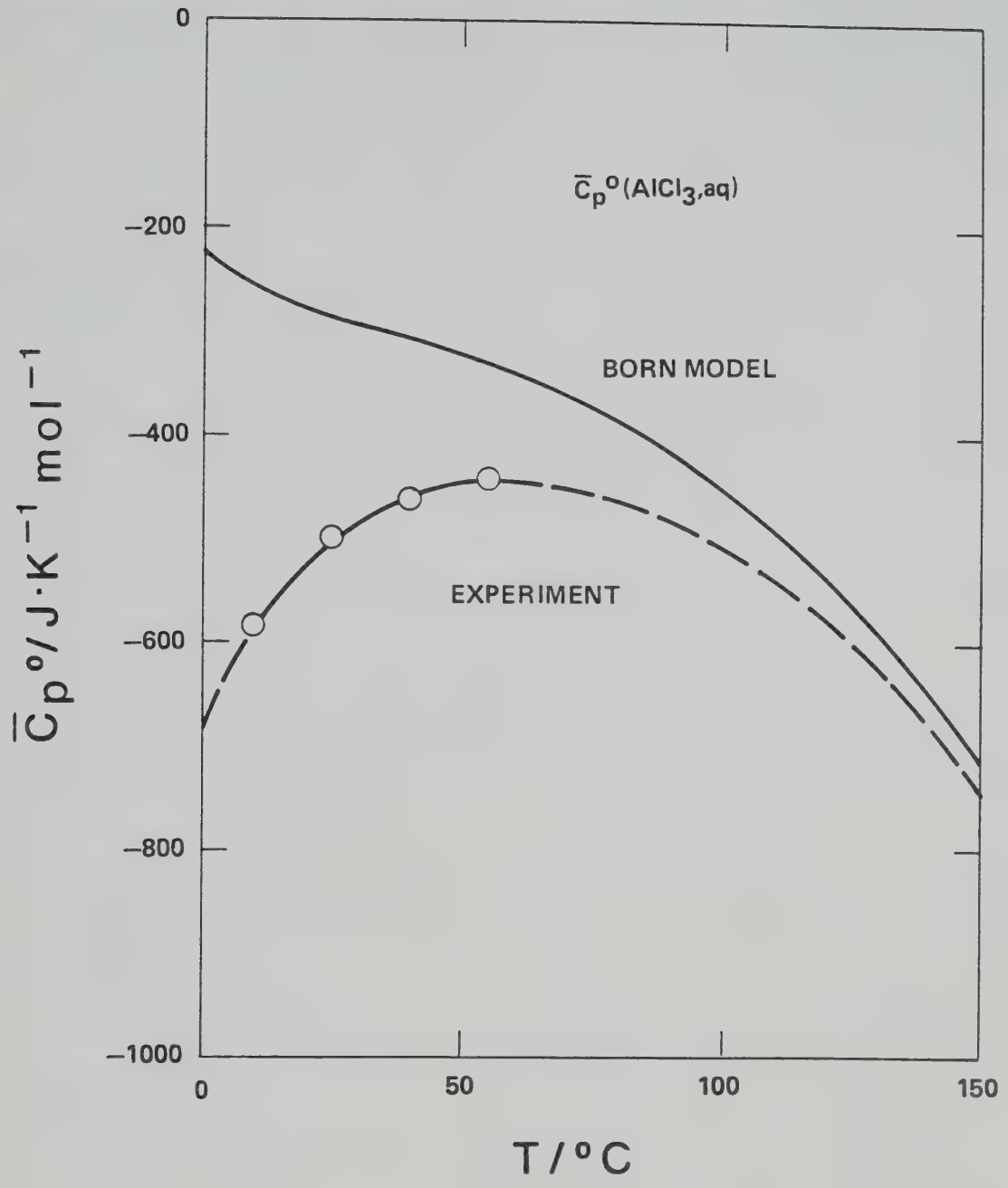

Figure 6.3: Experimental standard partial molar heat capacities for $AlCl_3$(aq) and the corresponding Born model function, ωTX. The broken curve is the extrapolated heat capacity function according to the Helgeson-Kirkham-Flowers model, eq. 6.20.

In principle, these data can be used to correlate excess or "relative" heat capacities in order to extrapolate activity and osmotic coefficients to elevated temperatures. These calculations pose certain complexities (PITZER and MAYORGA, 1974; PITZER, 1975). Some of these calculations have been addressed elsewhere (BARTA and HEPLER, 1986).

6.5 References

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Chapter 7

Thermodynamics of aqueous aluminate ion: Standard partial molar heat capacities and volumes of $Al(OH)_4^-(aq)$ from 10 to 55°C and related calculations[1]

7.1 Introduction

The thermodynamic properties of compounds of aluminum and of various aqueous ions of aluminum are useful in connection with several industrial applications and also many problems in geochemistry and the life sciences. As examples of areas in which thermodynamic properties of aqueous species of aluminum are useful, the following can be cited: soil chemistry, dissolution and precipitation reactions of minerals (including reactions that occur in the *in situ* recovery of bitumen from oil sands), hydrothermal ore body formation, geothermal power generation, and the corrosion of aluminum alloys in heat transfer systems. Many of these applications involve processes that operate at elevated temperature and pressure and often involve neutral or alkaline aqueous solutions in which the principal aluminum species are the hydroxy complexes.

There exist apparently reliable data for the thermodynamic properties of many aluminum minerals over a wide range of temperatures (see for example ROBIE *et al.* (1978). However, there have been troubling inconsistencies in the data for aluminum oxides, hydroxides, and simple aluminosilicates, which have caused uncertainties in the properties of aqueous aluminum species that are derived from solubility measurements. These uncertainties have been the subject of several recent investigations. The standard Gibbs free energy and entropy of the aluminum ion, $Al^{3+}(aq)$, are now

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well established at 25°C. The thermodynamic properties of the hydrolyzed species of aluminum at 25°C have been reviewed and critically evaluated by APPS *et al.* (1986, in preparation), BAES and MESMER (1976), COUTURIER *et al.* (1984), HEM (1986), HEMINGWAY (1982), and HEMINGWAY *et al.* (1978). Values for the equilibrium constants and enthalpies of the stepwise hydrolysis equilibria are moderately well known from solubility measurements below 100°C. Hydrolysis constants for the cationic hydroxy complexes have been measured to 300°C by potentiometric titrations (MACDONALD et al., 1973; MESMER and BAES, 1971). The anionic complex, $Al(OH)_4^-(aq)$, is the principal species in alkaline solutions at all temperatures. Its thermodynamic properties have been evaluated up to 300°C from solubility measurements on boehmite, gibbsite, and diaspore (APPS *et al.*, 1986).

It is desirable to have values for the standard state partial molar heat capacity and volume of aqueous aluminum species over a range of temperatures. These are derivative properties that are related to the temperature and pressure dependence of the Gibbs free energy and can be used to guide calculations of the complete thermodynamic surface for the aluminum-water system. Heat capacity and volume functions can also be used in empirical or semi-empirical treatments to extrapolate Gibbs free energies of formation to temperatures and pressures beyond the range of the measurements (MILLERO, 1979; CRISS and COBBLE, 1964a,b; HELGESON and KIRKHAM, 1976; HELGESON *et al.*, 1981).

Recent measurements that have yielded values for the standard state partial molar heat capacity and volume of $Al^{3+}(aq)$ from 10 to 55°C have been discussed in the preceding Chapter and in BARTA and HEPLER (1986). Of the monomeric hydroxy complexes of aluminum, only the aluminate ion, $Al(OH)_4^-(aq)$, can be obtained at high enough concentrations for direct heat capacity and volume measurements to be made. In addition, this is the most important aqueous species of aluminum present in alkaline solution.

The purpose of the present research has been to obtain the standard state partial molar heat capacity and volume of $Al(OH)_4^-(aq)$, or equivalently $AlO_2^-(aq)$, from 10 to 55°C, the range of temperature in which dramatic changes in these properties are known to take place. To do so, heat capacities and densities of aqueous solutions of the sodium salt in an excess of sodium hydroxide sufficient to avoid precipitation

of solid aluminum hydroxide have been measured. The presence of non-negligible concentrations of $Na^+(aq) + Al(OH)_4^-(aq)$ and $Na^+(aq) + OH^-(aq)$ in such solutions leads to complications in treating the experimentally measured quantities to obtain standard state properties and excess property functions. It is in this context that two different methods were used (Young's rule and the Pitzer ion interaction model) to account for the contribution of sodium hydroxide and thence obtain the desired thermodynamic properties of $Al(OH)_4^-(aq)$.

7.2 Experimental

Water used for all experiments was first passed through an activated charcoal filter, then through a Milli-RO4/Milli-Q reagent grade mixed bed ion exchange column and activated carbon system to achieve a final resistivity of 18 MΩ cm or greater. NaOH solutions were prepared from Fisher (certified, ACS) carbonate-free 50% solutions and standardized by titration against potassium hydrogen phthalate. Sodium oxohydroxo aluminate, $Na_6[Al_6O_4(OH)_{16}]$, was prepared from Fisher $Al(OH)_3$ (certified, ACS) by the method cited by BRAUER (1965). Briefly, the crystalline $Al(OH)_3$ was refluxed in a 50% aqueous solution of NaOH, then filtered to remove sodium carbonate. Crystalline sodium oxohydroxo aluminate was precipitated from the clear filtrate at 45°C, washed with 50% NaOH, methanol and acetone, then dried in a vacuum desiccator over silica gel.

Two stock solutions were prepared by adding the dry crystalline sodium oxohydroxo aluminate crystals to an excess of NaOH. One solution had a 1:2 mole ratio of $NaAl(OH)_4(aq)$ to NaOH(aq) and the second a 1:3 mole ratio. Aluminum in the stock solutions was determined gravimetrically by precipitation as the 8-hydroxyquinolate salt, as described by VOGEL (1978). Hydroxide in the stock solutions, m(NaOH) + $m[NaAl(OH)_4]$, was determined by titration with HCl to pH=7, at which point all of the aluminate was precipitated as $Al(OH)_3$. More dilute solutions were prepared by mass from the two standardized stock solutions. We note that the solubility of $Al(OH)_3(c)$ is proportional to the hydroxide molality above pH = 7 (BAES and MESMER, 1976) so that dilution of the stock solutions with water did not cause precipitation.

Heat capacities and volumes were measured relative to water with a Sodev model CP-C Picker flow microcalorimeter (PICKER it et al., 1971) and Sodev model 03D densimeter (PICKER *et al.*, 1974). The temperature of both instruments was controlled to ± 0.001°C with independent Sodev CT-L circulating baths. The temperatures were monitored with thermistors that had been calibrated with a Hewlett Packard 2804A quartz thermometer and placed just upstream of the measuring cells. Since the densities of the solutions were measured at each temperature, the calorimeter delay line was maintained at the cell temperature, and not independently controlled at 25°C as was described for the measurements on solutions containing Al^{3+}(aq) as described in the preceding Chapter.

The densimeter and calorimeter were calibrated with a standard 1 m NaCl solution, using density and heat capacity data from MILLERO (1970) and DESNOYERS *et al.* (1976), respectively. As a result of this calibration, the calorimetric measurements were corrected for a very small heat leak by the method of DESNOYERS *et al.* (1976) as described in Chapter 2. The correction factor was found to be $f = 1.004 \pm 0.002$ at 25°C and was assumed to be independent of temperature (TREMAINE *et al.*, 1986). The densities and specific heat capacities of water at 10, 25, 40 and 55°C were taken from KELL (1967, 1972), and had the values 0.999700, 0.997047, 0.992219, and 0.985695 g cm^{-3} and 4.1919, 4.1793, 4.1783, and 4.1821 J $K^{-1}g^{-1}$, respectively.

7.3 Results

7.3.1 Apparent Molar Properties

The measured relative densities $(d - d_1^\circ)$ and heat capacity-density ratios $\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$ for the $NaAl(OH)_4$/NaOH mixtures are listed in Table 7.1.

The notation used in Table 7.1 and elsewhere in this chapter follows the scheme (1 = H_2O, 2 = $NaAl(OH)_4$, and 3 = NaOH). The "experimental" apparent molar property ${}^{\phi}Y^{exp}$ of a solution is defined in terms of measured quantities as

$$ {}^{\phi}Y^{exp} = \frac{Y_{sol} - 55.509 Y_1^\circ}{m_2 + m_3} \tag{7.1} $$

where Y_{sol} is the extensive property (heat capacity or volume) of an amount of the

Table 7.1: Compositions of solutions and experimental apparent molar volumes and heat capacities for $NaAl(OH)_4/NaOH$ mixtures.

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d-d_1^\circ)$ (g cm^{-3})	ϕV^{exp} (cm^{3}mol^{-1})	$\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ}-1\right)$	ϕC_p^{exp} (J K^{-1}mol^{-1})
			10°C		
1.1709	2.3139	16.1803	17.01	1.562	91.34
0.8677	1.7148	12.5257	15.73	0.166	68.73
0.6697	1.3234	9.9619	14.74	−0.531	50.20
0.4523	0.8938	6.9708	13.47	−1.038	23.29
0.2746	0.5427	4.3621	12.28	−1.112	−6.55
0.1849	0.3653	2.9926	11.46	−0.957	−25.90
0.1210	0.2391	1.9870	10.81	−0.744	−42.26
0.08131	0.1607	1.3465	10.41	−0.550	−52.48
			25°C		
0.7207	2.2098	13.0190	12.97	1.374	74.55
0.4770	1.4625	9.0013	11.62	0.154	51.84
0.2870	0.8801	5.6229	10.31	−0.419	27.65
0.2088	0.6402	4.1546	9.72	−0.507	15.15
0.12508	0.3836	2.5320	9.05	−0.456	−0.27
0.07501	0.2300	1.5424	8.36	−0.341	−12.41
1.1709	2.3139	15.7473	18.09	2.392	106.10
0.8677	1.7148	12.1497	17.01	1.091	89.44
0.6697	1.3234	9.6426	16.17	0.369	75.44
0.4523	0.8938	6.7258	15.12	−0.216	56.11
0.2746	0.5427	4.1987	14.13	−0.444	35.74
0.1849	0.3653	2.8691	13.56	−0.430	23.30
0.1210	0.2391	1.8956	13.21	−0.352	13.63
0.08131	0.1607	1.2846	12.84	−0.269	6.50

Table 7.1: (continued)

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	$^{\phi}V^{exp}$ (cm^{3}mol^{-1})	$\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	$^{\phi}C_p^{exp}$ (J K^{-1}mol^{-1})
			40°C		
1.1709	2.3139	15.5305	18.55	2.916	114.41
0.8677	1.7148	11.9703	17.53	1.615	100.19
0.6697	1.3234	9.4710	16.85	0.861	88.65
0.4523	0.8938	6.6002	15.87	0.136	70.13
0.2746	0.5427	4.0950	15.20	−0.076	59.07
0.1849	0.3653	2.7931	14.75	−0.156	49.14
0.1210	0.2391	1.8312	14.81	−0.150	43.74
0.08131	0.1607	1.2401	14.49	−0.126	37.36
			55°C		
1.1709	2.3139	15.3909	18.78	3.216	118.81
0.8677	1.7148	11.8148	17.93	1.876	105.92
0.6697	1.3234	9.3851	17.08	1.151	95.54
0.4523	0.8938	6.5124	16.30	0.4756	82.39
0.2746	0.5427	4.0677	15.31	0.1163	69.18
0.1849	0.3653	2.7508	15.28	−0.0385	60.03
0.1210	0.2391	1.8157	15.00		
0.08131	0.1607	1.1994	15.96		

solution containing one kilogram of water, Y_1° is the molar heat capacity or volume of pure water, and m_2 and m_3 are the molalities of solutes 2 and 3, respectively. This equation is independent of the mixed electrolyte treatment chosen for analyzing the data. Experimental apparent molar volumes and heat capacities were calculated from the density and heat capacity results in Table 7.1 by the following equations:

$$\phi V^{exp} = \frac{\frac{1 + m_2 M_2 + m_3 M_3}{d} - \frac{1}{d_1^\circ}}{m_2 + m_3} \tag{7.2}$$

and

$$\phi C_p^{exp} = \frac{c_p(1 + m_2 M_2 + m_3 M_3) - c_{p,1}^\circ}{m_2 + m_3} \tag{7.3}$$

Here M is the molecular weight of the solute, c_p and d are the specific heat capacity and density of the solution, and $c_{p,1}^\circ$ and d_1° are the specific heat capacity and density of water, respectively. These experimental apparent molar properties are given in Table 7.1.

The data set at 25°C includes results from both the 1:2 and 1:3 $NaAl(OH)_4$/NaOH mixtures. The 1:2 ratio represents an excess of NaOH sufficient to avoid precipitation. The solutions with a 1:3 ratio contain a considerable additional excess of NaOH, and lead to data that will be useful later in our analysis of mixed electrolyte effects. Only the properties for the 1:2 mixtures were measured at temperatures other than 25°C.

The presence of excess hydroxide in the aluminate solutions requires that we use a model for excess properties to obtain standard state values for $Al(OH)_4^-(aq)$ from the experimental apparent molar properties of the mixtures. To ensure that the results are not strongly model dependent, we have chosen to calculate the properties for $Al(OH)_4^-(aq)$ (remove the contribution of NaOH) by two different methods. The first approach uses Young's rule (YOUNG and SMITH, 1954; REILLY and WOOD, 1969) and the second the Pitzer ion interaction approach (PITZER, 1973; PITZER, 1979; PITZER and KIM, 1974).

7.3.2 Excess Properties: Young's Rule

Young's rule (YOUNG and SMITH, 1954) expresses the apparent molar properties of mixtures in terms of those of the pure components at the same ionic strength as

that of the solution. For 1:1 electrolytes Young's rule can be written as

$$^{\phi}Y^{exp} = \frac{m_2}{m_2+m_3}{}^{\phi}Y_2 + \frac{m_3}{m_2+m_3}{}^{\phi}Y_3 + \delta_{23}^{Y} \tag{7.4}$$

Here δ_{23}^{Y} is a mixing term that is a function of solute molality and ionic strength. For 1:1 electrolytes, δ_{23}^{Y} has the form:

$$\delta_{23}^{Y} = k_{23}\frac{m_2 m_3}{(m_2+m_3)^2}I \tag{7.5}$$

The single adjustable constant, k_{23}^{Y}, is the solute binary interaction coefficient, which is evaluated by regression of our experimental results for solutions in which widely differing ratios of the two components were present.

Young's rule is most accurate for mixtures of 1:1 electrolytes with a common cation or anion (MILLERO, 1979; REILLY and WOOD, 1969). The present approach is similar to that in Chapter 6 for Al^{3+}(aq) except that the contribution of the pH controlling solute (NaOH) is very much larger here. As discussed in detail in Chapter 4, and as demonstrated in the preceding Chapter, the concentration dependence of $^{\phi}Y_2$ is represented in terms of the Guggenheim equation (MILLERO, 1979; PITZER and BREWER, 1961)

$$^{\phi}Y_2 = \bar{Y}_2^{\circ} + \omega A_Y(\frac{3}{2})\left(\frac{1}{\Lambda} - \frac{\sigma}{3}\right)I^{1/2} + B_Y I + C_Y I^{3/2} + D_Y I^2 \tag{7.6}$$

where

$$I = \omega m = \frac{1}{2}\sum m_i z_i^2 \tag{7.7}$$

$$\Lambda = 1 + I^{1/2} \tag{7.8}$$

$$\sigma = \frac{3\left(\Lambda - \frac{1}{\Lambda} - 2\ln\Lambda\right)}{I^{3/2}} \tag{7.9}$$

Values of the Debye-Hückel limiting slopes for apparent molar properties, A_Y (BRADLEY and PITZER, 1979), were taken from ANANTHASWAMY and ATKINSON (1984), and are listed in Table 7.3.

The apparent molar volumes and heat capacities of NaOH from 4 to 55°C are well established. Parameters for $^{\phi}Y_3$ were obtained by fitting the Guggenheim equation to NaOH data from 0 to 3 m (ROUX *et a;.*, 1984), using the Debye-Hückel limiting slopes cited above. The results of these fits are summarized in Table 7.2. With these results, we have optimized the parameters $B_{Y,2}$, $C_{Y,2}$ and k_{23}^{Y} by fits to the data in Table 7.1.

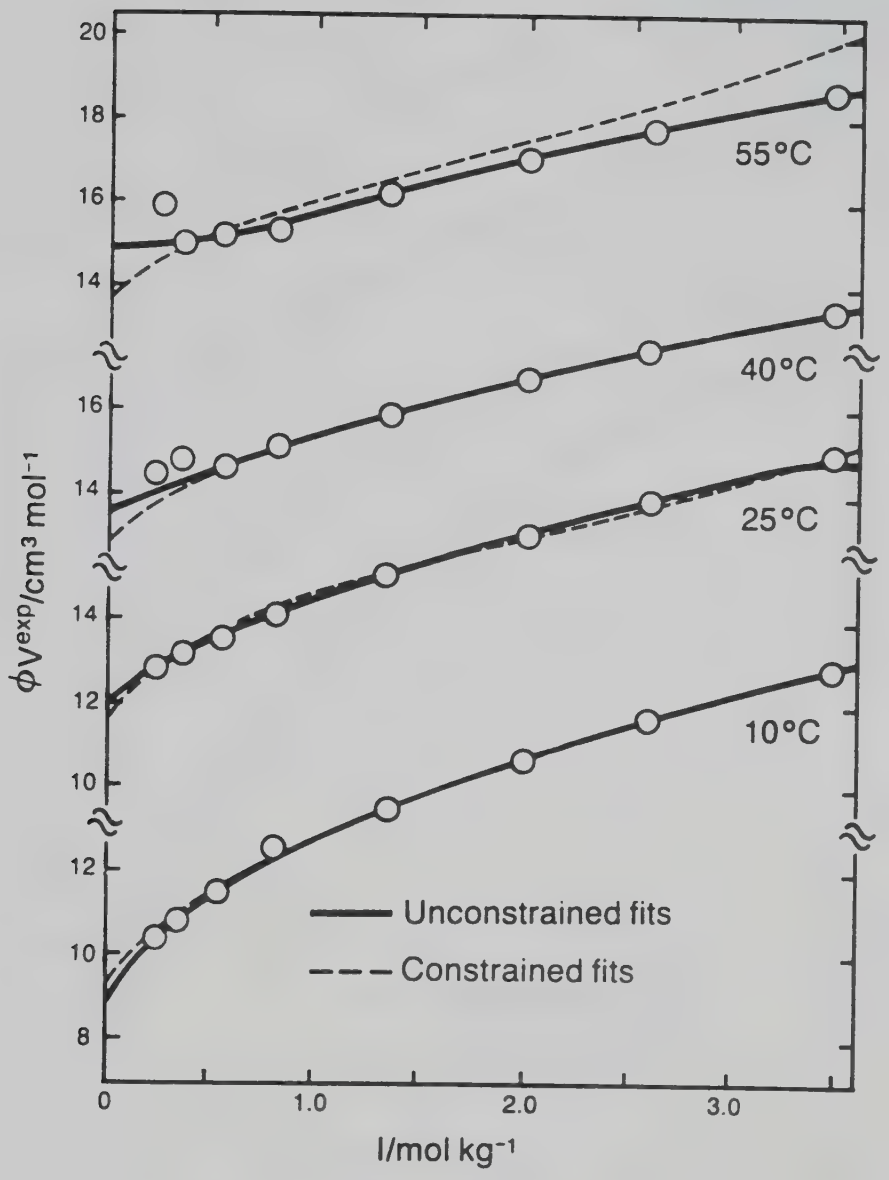

Figure 7.1: Experimental apparent molar volumes of aqueous $NaAl(OH)_4$ / NaOH mixtures vs ionic strength. The unconstrained fits from both models are identical except near infinite dilution where we arbitrarily show the limiting slopes from the Pitzer model. The dashed lines are fits from the Young's rule model with the Guggenheim B and C parameters constrained to eq. 7.10

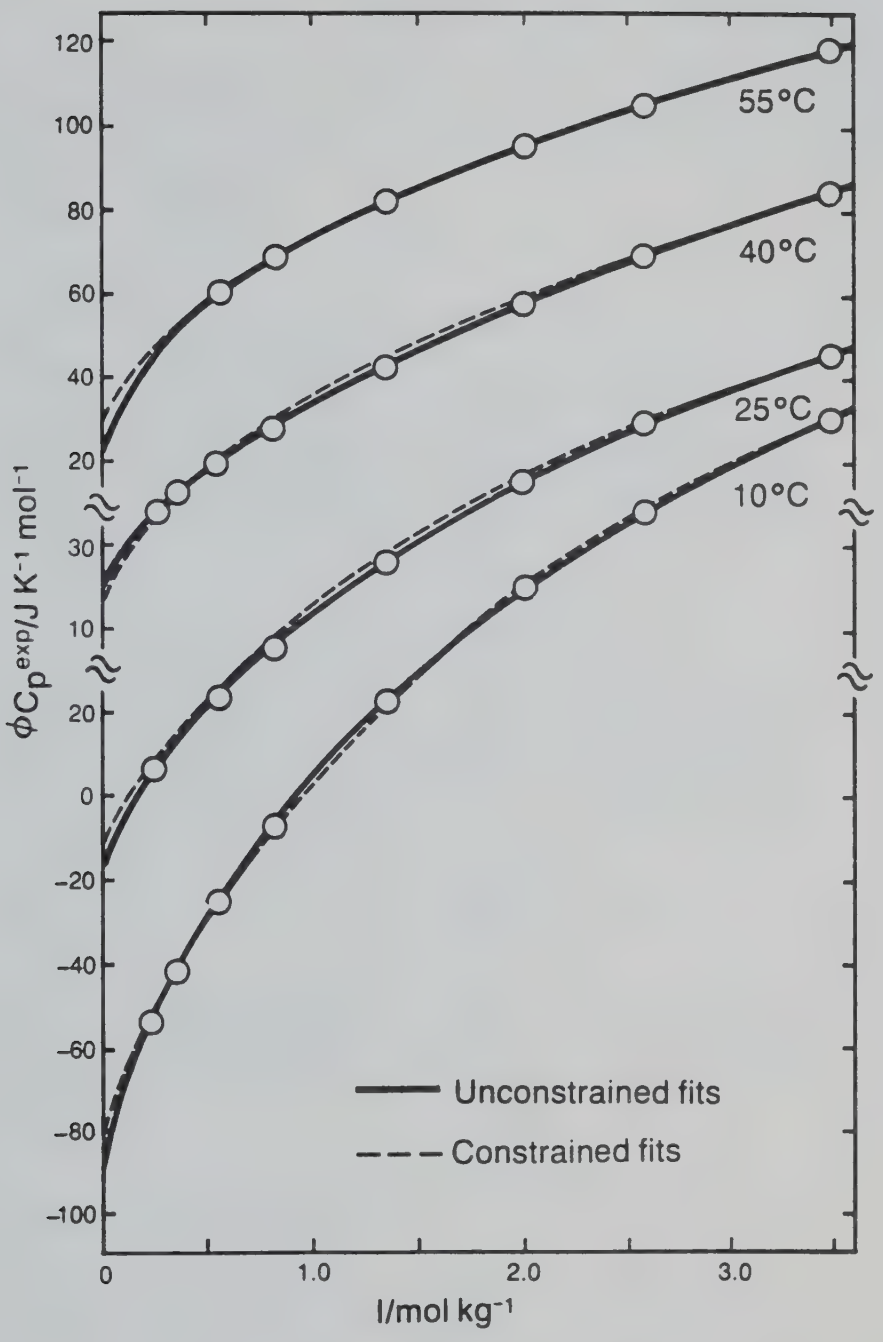

Figure 7.2: Experimental apparent molar heat capacities of aqueous $NaAl(OH)_4$ / NaOH mixtures vs ionic strength. The unconstrained fits from both models are identical except near infinite dilution where we arbitrarily show the limiting slopes from the Pitzer model. The dashed lines are fits from the Young's rule model with the Guggenheim B and C parameters constrained to eq. 7.10

Table 7.2: Limiting standard state partial molar volumes, heat capacities and concentration parameters for NaOH from the Guggenheim equation [ROUX *et al.* (1984)]* †

t (°C)	$\bar{V}_3^\circ$ ($cm^3 mol^{-1}$)	A_V ($cm^3 kg^{1/2} mol^{-3/2}$)	B_V ($cm^3 kg\ mol^{-2}$)	C_V ($cm^3 kg^{3/2} mol^{-5/2}$)	D_V ($cm^3 kg^2 mol^{-3}$)
4	-9.04 ± 0.02	1.5591	5.304 ± 0.29	-2.786 ± 0.42	0.5928 ± 0.15
10	-7.36 ± 0.02	1.6420	3.407 ± 0.26	-1.122 ± 0.38	0.1458 ± 0.13
25	-5.46 ± 0.10	1.8743	4.051 ± 0.82	-2.534 ± 1.09	0.6402 ± 0.37
40	-4.17 ± 0.22	2.1540	2.049 ± 0.08	-0.4590 ± 0.05	0
55	-3.41 ± 0.02	2.4946	1.363 ± 0.07	-0.1623 ± 0.04	0

t (°C)	${}^\phi C_{p,3}^\circ$ ($JK^{-1} mol^{-1}$)	A_C ($Jkg^{1/2} K^{-1} mol^{-3/2}$)	B_C ($J\ kg\ K^{-1} mol^{-2}$)	C_C ($J\ kg^{3/2} K^{-1} mol^{-5/2}$)
4	-215.05 ± 1.2	26.675	139.2 ± 3.6	-46.65 ± 3.6
10	-166.07 ± 0.5	28.446	101.3 ± 2.5	-31.79 ± 1.4
25	-97.49 ± 0.3	32.783	54.50 ± 0.6	-14.62 ± 0.6
40	-65.87 ± 0.2	37.446	33.90 ± 0.7	-7.425 ± 0.4
55	-51.21 ± 0.3	42.699	26.47 ± 0.8	-5.397 ± 0.4

* Although measurements were made on solutions having compositions up to 11 mol kg^{-1}, we have obtained the parameters here by restricting our least squares fits to data for solutions with $m < 3.026$ mol kg^{-1}.

† The uncertainties listed here correspond to statistical estimates of the standard deviations of each of the parameters.

The interaction coefficient k_{23}^{Y} was well defined by data for the two $NaAl(OH)_4$/NaOH ratios used at 25°C, and was found to be zero within statistical significance ($k_{23}^{V} = 0.9 \pm 2$ $cm^3 kg\ mol^{-2}$ and $k_{23}^{J} = 6 \pm 24$ J kg $K^{-1} mol^{-2}$; these uncertainties correspond to one standard deviation). On the basis of these calculations, k_{23} was taken to be zero at all temperatures. The values of the parameters B_Y and C_Y from our fits of eqs. 7.5 and 7.6 to the data at each temperature can be represented by polynomials of the form

$$B_Y(\text{ and } C_Y) = p_1 + p_2 T + p_3 T \tag{7.10}$$

without any significant loss in the accuracy of the fit to the experimental apparent molar properties. Here the coefficients, p_i, are adjustable parameters and T is the temperature in Kelvins. This quadratic constraint of the B and C terms did not affect the fitted infinite dilution properties. Table 7.3 lists the fitted values for $\bar{Y}_2^{\circ}$, $B_{Y,2}$ and $C_{Y,2}$ along with associated statistical uncertainties that correspond to fits with unconstrained B_Y and C_Y terms. The polynomial expressions for B_Y and C_Y are also included in Table 7.3.

The functions for ${}^{\phi}V^{exp}$ and ${}^{\phi}C_p^{exp}$ calculated from the fitted parameters are shown along with experimental data in Figures 7.1 and 7.2. Figures 7.3 and 7.4 are plots of experimental and calculated values of ${}^{\phi}V_2$ and ${}^{\phi}C_{p,2}$ for $NaAl(OH)_4$ at 25°C in which the Guggenheim form of the Debye-Hückel limiting law (given by eq. 7.6) has been subtracted from ${}^{\phi}V_2$ and ${}^{\phi}C_{p,2}$ for better definition of the limiting intercepts. The plots show the excellent agreement between values from solutions containing 1:2 and 1:3 ratios of $NaAl(OH)_4$ to NaOH. If the binary interactions represented by δ_{23}^{Y} in these solutions were significant, different values would have been obtained for the two different ratios of $NaAl(OH)_4$ and NaOH.

7.3.3 Excess Properties: Pitzer Ion Interaction Model

The Pitzer ion interaction approach (PITZER, 1973) has been used with success to represent the properties of both single and multicomponent electrolyte solutions to high ionic strengths (MILLERO, 1979; ROGERS, 1981; HARVIE and WEARE, 1980; PITZER, 1981; PITZER, 1986). The advantage of the Pitzer approach over the Young's rule method is the detailed consideration of specific ion interactions, which

Table 7.3: Standard state partial molar volumes and heat capacities for $NaAl(OH)_4$ and concentration parameters from Young's rule and the Guggenheim equation.*†

t (°C)	$\bar{V}_3^\circ$ ($cm^3 mol^{-1}$)	A_V ($cm^3 kg^{1/2} mol^{-3/2}$)	B_V ($cm^3 kg\ mol^{-2}$)	C_V ($cm^3 kg^{3/2} mol^{-5/2}$)
10	41.42 ± 0.14	1.6420	4.364 ± 0.32	-1.190 ± 0.17
25	45.06 ± 0.16	1.8743	1.835 ± 0.37	-0.282 ± 0.19
40	46.51 ± 0.35	2.1540	0.1722 ± 0.65	0.519 ± 0.31
55	47.20 ± 0.75	2.4946	-0.6253 ± 1.6	1.214 ± 0.77

t (°C)	${}^\phi C_{p,2}^\circ$ ($J K^{-1} mol^{-1}$)	A_J ($J kg^{1/2} K^{-1} mol^{-3/2}$)	B_J ($J\ kg\ K^{-1} mol^{-2}$)	C_J ($J\ kg^{3/2} K^{-1} mol^{-5/2}$)
10	80.9 ± 3.9	28.446	99.94 ± 9.1	-29.16 ± 4.6
25	138.7 ± 1.0	32.783	67.73 ± 2.4	-20.47 ± 1.4
40	171.9 ± 2.1	37.446	47.06 ± 4.0	-14.42 ± 2.0
55	178.5 ± 1.8	42.699	37.94 ± 3.3	-11.00 ± 1.6

* The uncertainties listed here correspond to statistical estimates of the standard deviations of each of the parameters from the unconstrained fits.

† $B_V = 214.47 - 1.2867T + 0.0019234T^2$ $cm^3 kg\ mol^{-2}$
$C_V = -38.26 + 0.1978T - 0.0002362T^2$ $cm^3 kg^{3/2} mol^{-5/2}$
$B_J = 2873.0 - 17.055T + 0.025646T^2$ $J\ K^{-1} kg\ mol^{-2}$
$C_J = -686.9 + 3.979T - 0.005849T^2$ $J\ K^{-1} kg^{3/2} mol^{-5/2}$

T is the absolute temperature: $T/K = t/°C + 273.15$.

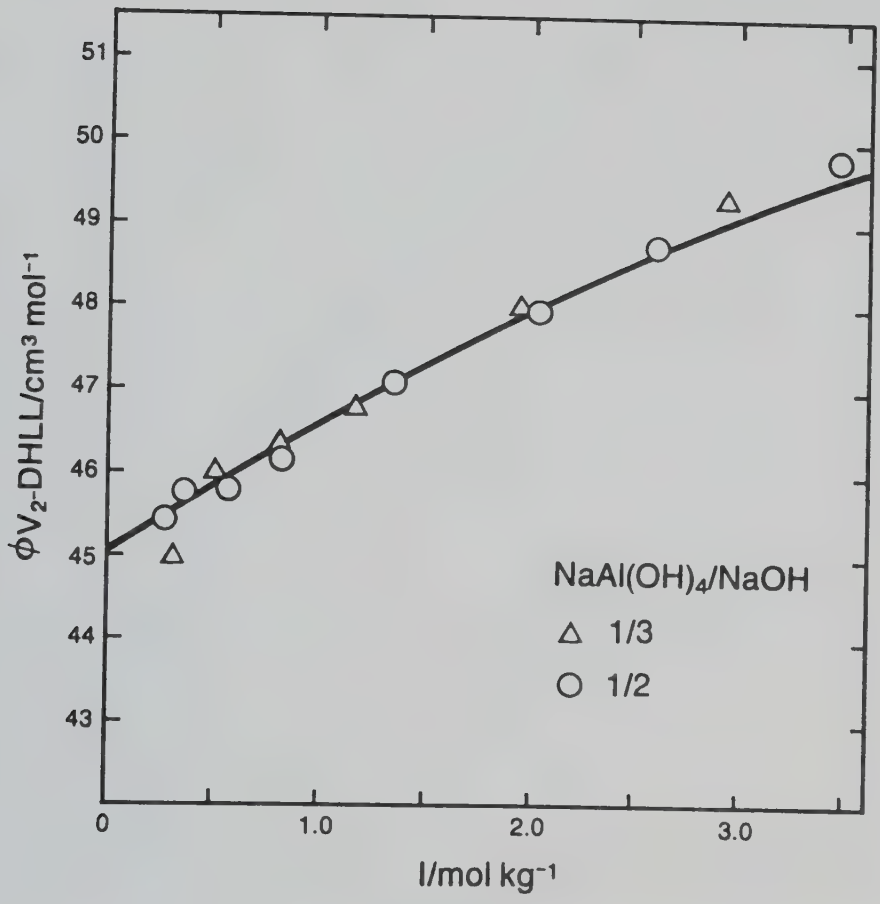

Figure 7.3: Apparent molar volumes of $NaAl(OH)_4$(aq) at 25°C derived from the Young's rule model for 1:2 and 1:3 ratios of $NaAl(OH)_4$ / NaOH after subtraction of the Debye-Hückel limiting law (DHLL) as given by the Guggenheim equation (eq. 7.6).

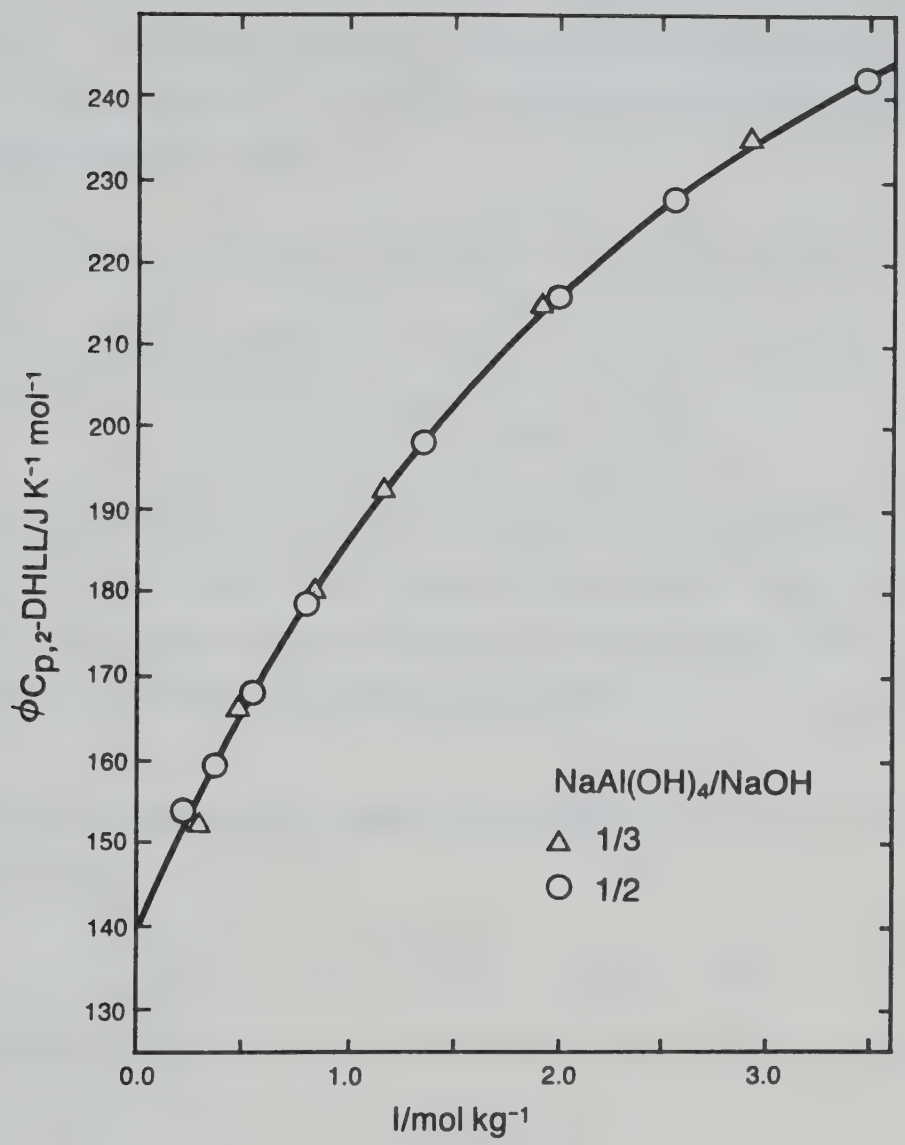

Figure 7.4: Apparent molar heat capacities of $NaAl(OH)_4(aq)$ at 25°C derived from the Young's rule model for 1:2 and 1:3 ratios of $NaAl(OH)_4$ / NaOH after subtraction of the Debye-Hückel limiting law (DHLL) as given by the Guggenheim equation (eq. 7.6)

become increasingly important at high ionic strengths.

The basic equation in the ion interaction approach considers the excess free energy to be the sum of long range electrostatic interactions (given by an extended Debye-Hückel theory) and specific short range binary and ternary interactions between ions (PITZER, 1973). The model yields the following equation for the excess free energy of a mixture containing two 1:1 electrolytes with a common cation (PITZER, 1979; PHUTELA and PITZER, 1986):

$$\frac{G^{EX}}{RT} = f(I)+2[m_c m_2(B_2+m_c C_2)+m_c m_3(B_3+m_c C_3)]+2m_2 m_3(\theta_{23}+m_c\frac{\psi_{23}}{2}) \quad (7.11)$$

Here, f(I) is the Pitzer form of the extended Debye-Hückel equation

$$f(I) = -A_\phi(\frac{4I}{1.2})\ln(1+1.2I^{1/2}) \quad (7.12)$$

and A_ϕ is the Debye-Hückel limiting slope for the osmotic coefficient. The B and C terms result from binary and ternary ion interactions, respectively. The terms θ_{23} and ψ_{23} arise from non-ideal mixing and are the result of binary and ternary ion interactions, respectively; m_c refers to the molality of the common cation ($m_c = m_2 + m_3$).

The excess volume and heat capacity are related to the experimental apparent molar properties by

$$Y^{EX} = (m_2+m_3)^\phi Y^{exp} - m_2\bar{Y}_2^\circ - m_3\bar{Y}_3^\circ \quad (7.13)$$

They can be derived from the excess Gibbs free energy, G^{EX}, by the following expressions:

$$V^{EX} = \left(\frac{\partial G^{EX}}{\partial p}\right)_T \quad (7.14)$$

$$C_p^{EX} = -T\left(\frac{\partial^2 G^{EX}}{\partial T^2}\right)_p \quad (7.15)$$

For solutions of a single 1:1 electrolyte (component 2 or 3 alone), the treatment yields the following equations (ROGERS and PITZER, 1982; SILVESTER and PITZER, 1977):

$$^\phi V = \bar{V}^\circ + (\frac{A_V}{1.2})\ln(1+1.2I^{1/2}) + 2RTB^V I + 2RTC^V I^2 \quad (7.16)$$

$$^\phi C_p = \bar{C}_p^\circ + (\frac{A_J}{1.2})\ln(1+1.2I^{1/2}) - 2RT^2B^J I - 2RT^2C^J I^2 \quad (7.17)$$

A_V and A_J are derived from eq. 7.12 after appropriate differentiation according to eqs. 7.14 and 7.15. C^Y is constant and B^Y is a function of ionic strength, which has the form

$$B^Y = \beta^{(0)Y} + 2\beta^{(1)Y}\frac{[1-(1+\alpha I^{1/2})\exp(-\alpha I^{1/2})]}{\alpha^2 I} \tag{7.18}$$

Here $\beta^{(0)Y}$ and $\beta^{(1)Y}$ are adjustable parameters and α is a constant set equal to 2.

For solutions of two 1:1 electrolytes, the equations for the experimental apparent molar properties can be represented in a form analogous to Young's rule:

$${}^{\phi}Y^{exp} = \frac{m_2}{m_2+m_3}{}^{\phi}Y_2 + \frac{m_3}{m_2+m_3}{}^{\phi}Y_3 + \delta^Y_{23} \tag{7.4}$$

The single component terms, ${}^{\phi}Y_2$ and ${}^{\phi}Y_3$, are described by eqs. 7.16 and 7.17. The interaction coefficients δ^Y_{23} can be written in terms of the excess mixing terms (BARTA and HEPLER, 1986; PITZER and KIM, 1974) from the Pitzer model:

$$\delta^V_{23} = RT\left[\left(\frac{2m_2m_3}{m_2+m_3}\right)\theta^V_{23} + m_2m_3(\psi^V_{23})^2\right] \tag{7.19}$$

$$\delta^J_{23} = -RT^2\left[\left(\frac{2m_2m_3}{m_2+m_3}\right)\theta^J_{23} + m_2m_3(\psi^J_{23})^2\right] \tag{7.20}$$

The term θ_{23} as defined by

$$\theta_{23} = \theta^{(0)} + 2\theta^{(1)}\frac{[1-(1+\alpha I^{1/2})\exp(-\alpha I^{1/2})]}{\alpha^2 I} \tag{7.21}$$

is similar in form to B, and ψ_{23} is an adjustable constant.

In this work the parameters for NaOH, ${}^{\phi}Y_3$, were obtained by fitting eqs. 7.16 and 7.17 to the data from ROUX *et al.* (1984) to obtain the values of $\bar{Y}_3^{\circ}$, $\beta_3^{(0)Y}$, $\beta_3^{(1)Y}$, and C_3^Y that are listed in Table 7.4. These parameters were then used in fitting eqs. 7.4 and 7.16 through 7.21 to the data in Table 7.1 to obtain the parameters for $NaAl(OH)_4$(aq); $\bar{Y}_2^{\circ}$, $\beta_2^{(0)Y}$, $\beta_2^{(1)Y}$, and C_2^Y, and the excess mixing terms $\theta^{(0)}_{23}$, $\theta^{(1)}_{23}$, and ψ^Y_{23}. As in the Young's rule approach, the interaction coefficients are defined by the two different $NaAl(OH)_4$/NaOH ratios at 25°C. PITZER (1975) has noted that θ_{23} is often independent of ionic strength, thus giving a zero value to $\theta^{(1)}_{23}$. Also, the parameter resulting from non-ideal ternary ion interactions, ψ^Y_{23}, is usually important only for relatively high ionic strengths. In our analysis, least squares fits that included any of the mixing terms $\theta^{(0)}_{23}$, $\theta^{(1)}_{23}$, and ψ^Y_{23} gave no smaller standard deviation than did fits with just the parameters for pure component 2. The mixing

terms were therefore set equal to zero at all temperatures. The results of these fits are presented in Table 7.5. Polynomial fits to the temperature dependence of $\beta_2^{(0)Y}$, $\beta_2^{(1)Y}$, and C_2^Y terms did not satisfactorily represent the experimental data and are not reported.

The standard state properties and B_2^Y parameters were also fitted without including the C_2^Y parameter and the results are included in Table 7.5. The overall variance was significantly larger in most cases than that of the four parameter fit described above, and it is considered that the C_2^Y terms are necessary to describe the results accurately.

7.3.4 Standard State Properties

Neither the Young's rule model (using the Guggenheim forms of the apparent molar properties) nor the Pitzer ion interaction model requires mixing terms to describe the apparent molar properties reported here. We attribute this to the presence of Na^+ as a common cation and to the similarity of the anionic species. The aluminate ion, $Al(OH)_4^-$, has been shown to be tetrahedrally bound by hydroxy ligands (MOLENAAR *et al.*, 1970; BROOKER *et al.*, 1988). The tetrahedral structure of $Al(OH)_4^-$ suggests that interactions of this ion with Na^+ and other ions may be similar to such interactions by OH^-. The difference between the two models is therefore entirely due to the choice of the Guggenheim or Pitzer representation of the excess properties of the pure components (eqs. 7.6, 7.16 and 7.17, respectively).

The standard state properties derived from the Young's rule/Guggenheim treatment listed in Table 7.3 have been chosen as the preferred values. This treatment gave smaller deviations than those obtained from either the three parameter or four parameter Pitzer model. In addition, the temperature dependence of the excess property parameters is conveniently represented by the polynomial coefficients listed in Table 7.3.

The equation used to represent the temperature dependence of the standard partial molar properties for $Al(OH)_4^-(aq)$ is of the form used by HOLMES and MESMER (1983) to represent the standard state properties of the alkali metal halides:

$$\bar{Y}_2^\circ = a + \frac{b}{T-\theta} + cT + dT^2 \qquad (7.22)$$

Table 7.4: Values of parameters from the Pitzer model for NaOH data from ROUX *et al.* (1984).*

t (°C)	$\bar{V}_3^\circ$ (cm^3mol^{-1})	$10^3\beta_3^{(0)V}$ (kg $mol^{-1}bar^{-1}$)	$10^3\beta_3^{(1)V}$ (kg $mol^{-1}bar^{-1}$)	$10^4C_3^V$ ($kg^2mol^{-2}bar^{-1}$)
		Volume		
4	-9.10 ± 0.02	3.412 ± 0.080	11.30 ± 0.52	-1.142 ± 0.061
10	-7.42 ± 0.03	3.146 ± 0.093	6.881 ± 0.60	-1.042 ± 0.071
25	-5.47 ± 0.06	2.235 ± 0.12	6.433 ± 0.91	-0.597 ± 0.090
40	-4.21 ± 0.02	1.932 ± 0.049	3.128 ± 0.33	-0.484 ± 0.037
55	-3.45 ± 0.04	1.731 ± 0.054	0.935 ± 0.45	-0.432 ± 0.039
t (°C)	${}^\phi C_{p,3}^\circ$ ($JK^{-1}mol^{-1}$)	$10^5\beta_3^{(0)J}$ (kg $mol^{-1}K^{-2}$)	$10^4\beta_3^{(1)J}$ (kg $mol^{-1}K^{-2}$)	$10^6C_3^J$ ($kg^2mol^{-2}K^{-3}$)
		Heat Capacity		
4	-220.41 ± 2.0	2.070 ± 0.24	1.920 ± 0.16	-1.092 ± 0.18
10	-170.39 ± 1.6	1.813 ± 0.17	1.281 ± 0.11	-0.939 ± 0.12
25	-100.99 ± 1.1	1.307 ± 0.071	0.5284 ± 0.054	-0.630 ± 0.053
40	-67.06 ± 0.64	1.031 ± 0.040	0.1895 ± 0.029	-0.483 ± 0.030
55	-52.97 ± 0.71	0.7698 ± 0.026	0.1278 ± 0.023	-0.345 ± 0.018

* The uncertainties listed here correspond to statistical estimates of the standard deviations of each of the parameters.

Table 7.5: Values of parameters from the Pitzer model for $NaAl(OH)_4/NaOH$ mixtures.*

t (°C)	$\bar{V}_2^\circ$ (cm^3mol^{-1})	$10^3\beta_2^{(0)V}$ (kg $mol^{-1}bar^{-1}$)	$10^2\beta_2^{(1)V}$ (kg $mol^{-1}bar^{-1}$)	$10^4C_2^V$ ($kg^2mol^{-2}bar^{-1}$)
		Volume		
10	40.90 ± 0.31	4.226 ± 1.4	1.278 ± 0.64	-3.233 ± 2.4
	40.56 ± 0.19	2.307 ± 0.23	2.091 ± 0.23	0
25	45.72 ± 0.38	6.193 ± 1.7	-1.495 ± 0.76	-6.043 ± 2.9
	45.15 ± 0.18	2.765 ± 0.64	-0.1199 ± 0.18	0
40	48.65 ± 1.7	5.815 ± 4.4	-2.767 ± 2.4	-5.225 ± 6.5
	47.40 ± 0.64	2.363 ± 0.44	-0.9217 ± 0.57	0
55	51.11 ± 1.9	13.54 ± 6.1	-6.810 ± 3.0	-17.10 ± 9.7
	48.20 ± 1.2	2.904 ± 0.99	-18.14 ± 1.1	0
t (°C)	$\bar{C}_{p,2}^\circ$ ($JK^{-1}mol^{-1}$)	$10^6\beta_2^{(0)J}$ (kg $mol^{-1}K^{-2}$)	$10^5\beta_2^{(1)J}$ (kg $mol^{-1}K^{-2}$)	$10^6C_2^J$ ($kg^2mol^{-2}K^{-3}$)
		Heat Capacity		
10	57.8 ± 6.8	-10.91 ± 12	-20.17 ± 5.1	-0.4884 ± 1.9
	59.2 ± 3.5	-13.80 ± 1.5	-18.95 ± 1.5	0
25	136.8 ± 2.9	-25.65 ± 4.4	-3.003 ± 1.9	2.953 ± 0.75
	127.3 ± 2.5	-8.429 ± 1.0	-10.24 ± 0.99	0
40	189.8 ± 13.7	-18.30 ± 19	4.011 ± 8.3	1.278 ± 3.1
	185.2 ± 6.9	-10.75 ± 2.5	0.8418 ± 2.5	0
55	164.2 ± 7.4	2.323 ± 5.5	7.769 ± 3.0	1.028 ± 0.84
	172.7 ± 3.4	-4.476 ± 0.68	-4.133 ± 0.87	0

* The uncertainties listed here correspond to statistical estimates of the standard deviations of each of the parameters.

In earlier investigations such as those discussed in Chapter 6, or in TREMAINE *et al.* (1986), eq. 7.22 was found to fit heat capacity data for both HCl(aq) and $AlCl_3$(aq) to within experimental uncertainty when θ was set equal to 190 K. For $NaAl(OH)_4$(aq), however, the experimental heat capacities were found to be much better represented by the a, c and d parameters alone. The equations for $NaAl(OH)_4$(aq) are

$$\bar{V}_2^\circ[\mathrm{NaAl(OH)_4,\ aq}] = 170.14 - \frac{5020.8}{T - 190} - 0.26408T \tag{7.23}$$

and

$$\bar{C}_{p,2}^\circ[\mathrm{NaAl(OH)_4,\ aq}] = -5798.2 + 36.802T - 0.056644T^2 \tag{7.24}$$

To calculate the standard state properties for $Al(OH)_4^-$(aq), data for HCl(aq) and NaCl(aq) must be combined with the present results for $NaAl(OH)_4$(aq). The recent volumetric data for HCl(aq) from HERRINGTON *et al.* (1985) and ALLRED and WOOLLEY (1981) have been chosen in preference to the data from AKERLOF and TEARE (1938), that cover a broader temperature range but are inconsistent with the more recent results. We have also chosen to use the expression reported by TREMAINE *et al.* (1986) for the heat capacity of HCl(aq). The expressions for the volume and heat capacity of NaCl(aq) were obtained from fits to the very precise data of MILLERO (1970), PERRON *et al.* (1975) and DESNOYERS *et al.* (1976). The results are summarized below:

$$\bar{V}_2^\circ(\mathrm{NaCl,\ aq}) = 62.333 - 0.09108T - \frac{2012.8}{T - 190}\ ;\ 0 \text{ to } 55^\circ\mathrm{C} \tag{7.25}$$

$$\bar{C}_{p,2}^\circ(\mathrm{NaCl,\ aq}) = 1885.0 - 4.305T - \frac{73838}{T - 190}\ ;\ 1 \text{ to } 45^\circ\mathrm{C} \tag{7.26}$$

$$\bar{V}_2^\circ(\mathrm{HCl,\ aq}) = 73.549 - 0.12799T - \frac{1897.9}{T - 190}\ ;\ 10 \text{ to } 75^\circ\mathrm{C} \tag{7.27}$$

$$\bar{C}_{p,2}^\circ(\mathrm{HCl,\ aq}) = 582.2 - 1.467T - \frac{29356}{T - 190}\ ;\ 10 \text{ to } 140^\circ\mathrm{C} \tag{7.28}$$

Combining the above equations leads to

$$\bar{V}_2^\circ[\mathrm{Al(OH)_4^-,\ aq}] = 173.71 - 0.2844T - \frac{4617.9}{T - 190} \tag{7.29}$$

and

$$\bar{C}_{p,2}^\circ[\mathrm{Al(OH)_4^-,\ aq}] = -7101.0 + 39.64T - \frac{27343}{T - 190} - 0.05664T^2 \tag{7.30}$$

Equilibrium calculations involving these ions over the specified temperature ranges should employ these functions rather than the high temperature extrapolations that are given in the following section.

Standard partial molar properties on the conventional scale [$\bar{V}°(H^+, aq) \equiv 0$; $\bar{C}_p°(H^+, aq) \equiv 0$] are listed in Table 7.6 for each of the ions cited here at each experimental temperature. Values for the Gibbs free energy of formation and entropy of $Al^{3+}(aq)$, $Al(OH)_4^-(aq)$ and other key ions are included in Table 7.7 for use in calculations that follow.

7.4 Discussion

7.4.1 Correlations for 25°C

The standard state volumes and heat capacities for $Al(OH)_4^-(aq)$ in Table 7.6 are the first experimental values reported for any anionic metal-hydroxy complex. These new values permit comparisons with predictive schemes that have been used in the past to estimate the thermodynamic properties of $Al(OH)_4^-(aq)$ and other hydrolyzed metal ions.

There are many semi-empirical models that relate standard state partial molar properties of various monomeric cations and anions to charge, radius and other parameters. However, no models have been developed specifically for hydrolyzed metal ionic species. BROOK (1972) and MACDONALD and BUTLER (1972) have estimated the properties of $Al(OH)_4^-(aq)$ from correlations developed for oxyanions by using the formula $\bar{Y}°(AlO_2^-, aq) = \bar{Y}°[Al(OH)_4^-, aq] - 2\bar{Y}°(H_2O, l)$. This approach has been widely used for other ions and merits a careful examination. In their approach the conventional standard state entropy $\bar{S}°$ (AlO_2^-, aq) was estimated to be *96.4* J $K^{-1}mol^{-1}$ from the equation of CONNICK and POWELL (1973). This entropy was then used in the entropy correspondence principle relationship of CRISS and COBBLE (1964a,b)

$$\bar{C}_p°(\text{oxyanions})/(\text{J K}^{-1}\text{mol}^{-1}) = -607 + 2.20(\bar{S}° - 20.9z) - 117z \qquad (7.31)$$

to yield the value for $\bar{C}_p°$ $[Al(OH)_4^-, aq] = \bar{C}_p°$ $(AlO_2^-, aq) + 2$ $\bar{C}_p°$ (H_2O, l) = *-81* J $K^{-1}mol^{-1}$. The same calculation with the entropy calculated from experimental

Table 7.6: Standard (conventional) partial molar volumes and heat capacities.*

	$\bar{V}°/(\mathrm{cm^3 mol^{-1}})$				
$t/°\mathrm{C}$	H^+	Cl^-	Na^+	Al^{3+}	$Al(OH)_4^-$
10	0	17.15	−2.21	−43.2	43.6
25	0	17.89	−1.27	−44.7	46.3
40	0	17.91	−0.44	−45.7	47.0
55	0	17.81	0.12	−47.4	47.3

	$\bar{C}_p°/(\mathrm{J\ K^{-1} mol^{-1}})$				
$t/°\mathrm{C}$	H^+	Cl^-	Na^+	Al^{3+}	$Al(OH)_4^-$
10	0	−148.4	21.8	−138.1	59.1
25	0	−126.6	42.2	−119.5	96.5
40	0	−115.5	52.8	−110.4	119.1
55	0	−111.7	49.5	−108.1	129.0

* The values reported here were taken from Chapter 6, BARTA and HEPLER (1986), TREMAINE *et al.* (1986), MILLERO (1970), ALLRED and WOOLLEY (1981), and PERRON *et al.* (1975) at original measurement temperatures or from eqs. 7.25-7.27 for intermediate values. The values for $Al(OH)_4^-(aq)$ are from this work. The accuracies of these reported values are $\pm$ 0.3 $\mathrm{cm^3 mol^{-1}}$ for $\bar{V}°$ and $\pm$ 3 $\mathrm{J\ K^{-1} mol^{-1}}$ for $\bar{C}_p°$ for the 1:1 electrolytes and slighter larger for $Al^{3+}(aq)$. Our estimated accuracies for the properties of $Al(OH)_4^-(aq)$ are discussed in the text.

Table 7.7: Standard state Gibbs free energies of formation and entropies at 25°C.

Species	ΔG_f° kJ mol^{-1}	$\bar{S}^\circ$ J K^{-1}mol^{-1}	Reference
Al^{3+}(aq)	−489.4*	−308.*	HEMINGWAY *and* ROBIE (1977)
$Al(OH)_4^-$(aq)	−1304.83*	123.8*	APPS *et al.* (in prep.)
Na^+(aq)	−261.905	59.0	WAGMAN *et al.* (1982)
Cl^-(aq)	−131.228	56.5	WAGMAN *et al.* (1982)
OH^-(aq)	−157.244	−10.75	WAGMAN *et al.* (1982)
H^+(aq)	0	0	

* These values are much more uncertain than the other values listed and have associated errors of about ± 1 kJ mol^{-1} and ± 10 J K^{-1}mol^{-1} for ΔG_f° and $\bar{S}^\circ$ respectively. WAGMAN *et al.* (1982) list the value $\bar{S}^\circ[Al(OH)_4^-, \text{ aq}] = 102.9$ J K^{-1}mol^{-1}.

results of COUTURIER *et al.* (1986), $\bar{S}^\circ$ (AlO_2^-, aq) = 1.85 J $K^{-1}mol^{-1}$ that leads to $\bar{C}_p^\circ$ [$Al(OH)_4^-$, aq] = *-289* J $K^{-1}mol^{-1}$. Neither estimate agrees well with the experimental value of $\bar{C}_p^\circ$ [$Al(OH)_4^-$, aq] = 96.5 J $K^{-1}mol^{-1}$.

Recent meaurements have led to a reported a value for $\bar{V}^\circ$[$Al(OH)_4^-$, aq] of 42.3 ± 1.7 cm^3mol^{-1} (SANJUAN and MICHARD, 1988) compared with the present value 46.3 ± 0.3 cm^3mol^{-1}. These measurements, although obtained both as a function of hydroxide and aluminate concentrations, show much larger scatter than do the present results. It also seems that the densimetric measurements by these authors did not reflect account of the difficulties associated with using densimeters equipped with platinum cells (see discussion in HOVEY and TREMAINE, 1985). For these reasons, the present result is considered more reliable.

COUTURE and LAIDLER (1957) have reported a correlation that relates the apparent molar volumes of oxyanions to their charge (z), radius ($r/\AA$), and the number of charge bearing ligands (n):

$$\bar{V}^\circ(\text{oxyanions})/(\text{cm}^3\text{mol}^{-1}) = 58.5 + 0.89(0.25nr)^3 - 26 \mid z \mid \qquad (7.32)$$

The value $r = 3.31\AA$, obtained by summing the Pauling interionic distances plus the van der Waals radius of the oxygen atom, yields $\bar{V}^\circ$ [$Al(OH)_4^-$, aq] = $\bar{V}^\circ$ (AlO_2^-, aq) + $2\bar{V}^\circ$ (H_2O, l) = *73* cm^3mol^{-1}. This prediction is in rather poor agreement with the experimental result in Table 7.6, 46.3 cm^3mol^{-1}.

On the basis of these comparisons, there is little justification for estimating standard partial molar heat capacities, volumes, and entropies of anionic hydroxy complexes from correlations developed to date for oxyanions.

7.4.2 Extrapolations to elevated temperatures

HELGESON and KIRKHAM (1976) and HELGESON *et al.* (1981), have described the temperature and pressure dependence of $\bar{C}_p^\circ$ and $\bar{V}^\circ$ in terms of a semi-empirical model based on the Born equation for ion-water interaction. The model has been used with success in fitting most of the limited results that were available at the time the work was done, and in extrapolating such results to higher temperatures (TREMAINE *et al.*, 1986).

The model postulates the temperature and pressure dependence of the standard state volume as

$$\bar{V}^{\circ}_{T} = \sigma + \frac{\xi T}{T - \theta} + \Delta V_{BORN} \tag{7.33}$$

where

$$\sigma = a_1 + a_2 p \tag{7.34}$$

and

$$\xi = a_3 + a_4 p \tag{7.35}$$

and similarly for heat capacity:

$$\bar{C}^{\circ}_{p,T} = c_1 + \frac{c_2 T}{T - \theta} + \Delta C_{p,BORN} \tag{7.36}$$

The term $T - \theta$ represents the non-electrostatic contributions to the partial molar properties, that increase sharply from 0 to about 80°C. The Born term describes the long range solvent polarization, and becomes the dominant term at very high temperatures. The equations for these Born terms are listed below:

$$\Delta V_{BORN} = -\omega Q \tag{7.37}$$

$$\Delta C_{p,BORN} = \omega T X \tag{7.38}$$

where

$$Q = \left(\frac{\partial \ln \epsilon}{\partial p}\right)_T \tag{7.39}$$

$$X = \frac{1}{\epsilon}\left[\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_p - \left(\frac{\partial \ln \epsilon}{\partial T}\right)_p^2\right] \tag{7.40}$$

$$\omega/(\text{J mol}^{-1}) = 6.9466 \times 10^5 \frac{z^2}{r}\text{Å} \tag{7.41}$$

Here ϵ is the static dielectric constant of water, z is the charge of the ion, and r is the "effective" radius. For monatomic anions the effective radius is the Pauling crystallographic radius and for cations it is the crystallographic radius plus 0.94 Å. Values of X and Q are given in the tabulations of HELGESON and KIRKHAM (1974) and HELGESON and KIRKHAM (1976), respectively.

The effective radius used for $Al(OH)_4^-$(aq) was estimated to be 3.31 Åby adding the radius of Al^{3+} to the diameter of one water molecule or OH^- ion. Least squares fits to the standard state volumes and heat capacities in Table 7.3 yield the following

expressions, which are plotted along with the experimental results in Figures 7.5 and 7.6.

$$\bar{V}^{\circ}_{2,T}[\mathrm{NaAl(OH)_4,\ aq}]/(\mathrm{cm^3 mol^{-1}}) = 57.073 - \frac{1.2803\ T}{T - 254} - 5.7356 \times 10^6 Q \quad (7.42)$$

$$\bar{C}_{p,2,T}[\mathrm{NaAl(OH)_4,\ aq}]/(\mathrm{J\ K^{-1} mol^{-1}}) = 338.17 - \frac{21.375\ T}{T - 254} + 5.7356 \times 10^5 TX \quad (7.43)$$

Here $\bar{V}^{\circ}_{2,T}$ and $\bar{C}^{\circ}_{p,2,T}$ are in $\mathrm{cm^3 mol^{-1}}$ and $\mathrm{J\ K^{-1} mol^{-1}}$, respectively; Q and X are in units of $\mathrm{bar^{-1}}$ and $\mathrm{K^{-2}}$, respectively.

The high temperature equilibrium calculations that follow in the next section require similar extrapolations for HCl(aq) and NaOH(aq). These functions have been reported by HELGESON *et al.* (1981), but more recent data can be used for such calculations.

For HCl(aq), volumetric data from HERRINGTON *et al.* (1985) and ALLRED and WOOLLEY (1981), were used instead of the data from AKERLOF and TEARE (1938) or ELLIS and MCFADDEN (1968) to generate the extrapolation equations. The heat capacity parameters for HCl(aq) were taken from TREMAINE *et. al.* (1986). It was not possible to use the same value of θ to fit both the volume and heat capacity functions for HCl(aq); therefore independent values θ_V and θ_J were assigned. BARTA and HEPLER (1986), reported a fit of the HKF model to low temperature volumetric data for $AlCl_3$(aq). In their fits they chose to calculate the Born terms from a different source of dielectric constant data. Their experimental results have been refitted using the Born terms from HELGESON and KIRKHAM (1976). The results of the fits to these data are summarized in Table 7.8.

The parameters in Table 7.8 were used in calculating the Gibbs free energies of formation of $Al(OH)_4^-$(aq) by the following method. Values of the Gibbs free energies referenced to the elements at 298.15 K and 1 bar for $NaAl(OH)_4$(aq) and HCl(aq), were obtained by integrating the expression

$$\Delta G^{\circ}_T = \Delta G^{\circ}_{f,298} - \bar{S}^{\circ}_{298}(T - 298.15) + \int_{298}^{T} \bar{C}^{\circ}_p dT - T \int_{298}^{T} \frac{\bar{C}^{\circ}_p}{T} dT + \int_1^p \bar{V}^{\circ} dp \quad (7.44)$$

using the formulas given by HELGESON *et al.* (1981) and the values for $\Delta G^{\circ}_{f,298}$ and $\bar{S}^{\circ}_{298}$ listed in Table 7.7. The Gibbs free energies of the aluminate ion referenced to the elements at T were then calculated by combining the values for $NaAl(OH)_4$(aq)

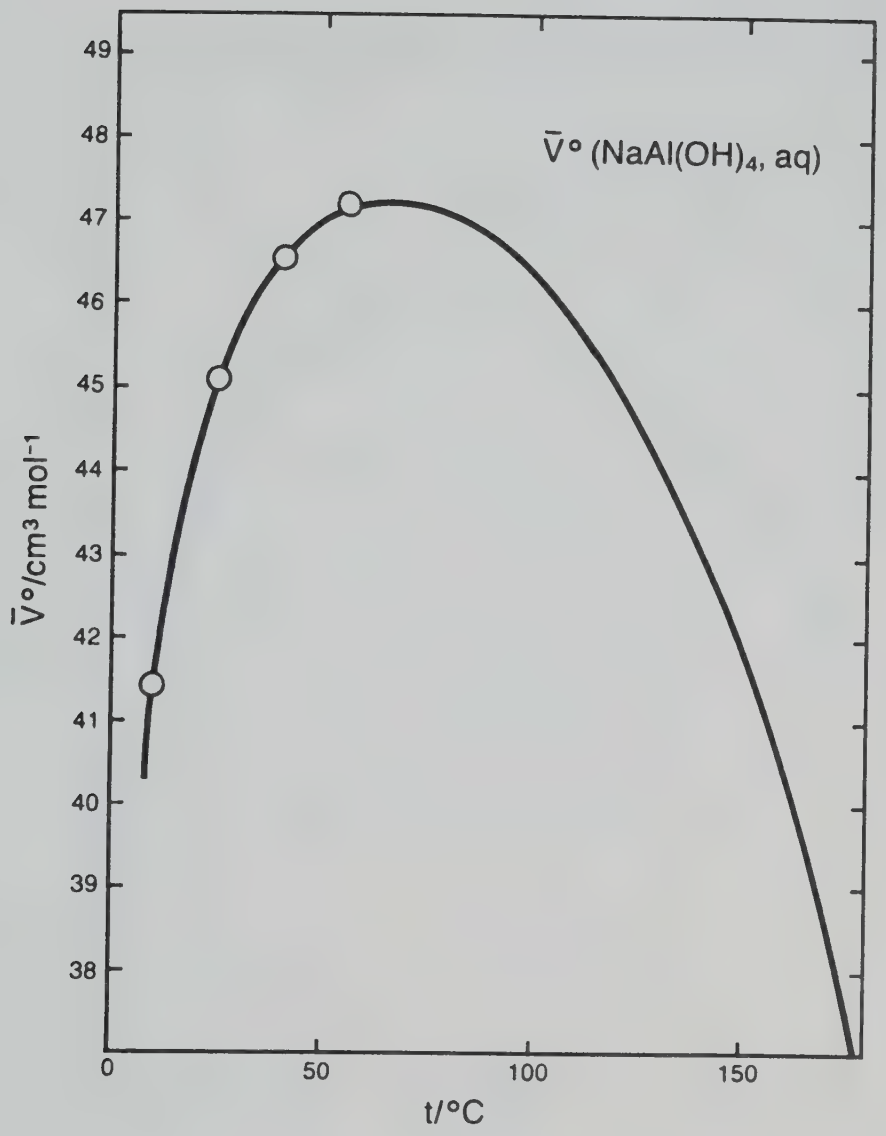

Figure 7.5: Standard state volumes for $NaAl(OH)_4(aq)$. The solid line is the extrapolation produced from a fit of the Helgeson-Kirkham-Flowers model to the 10-55°C data.

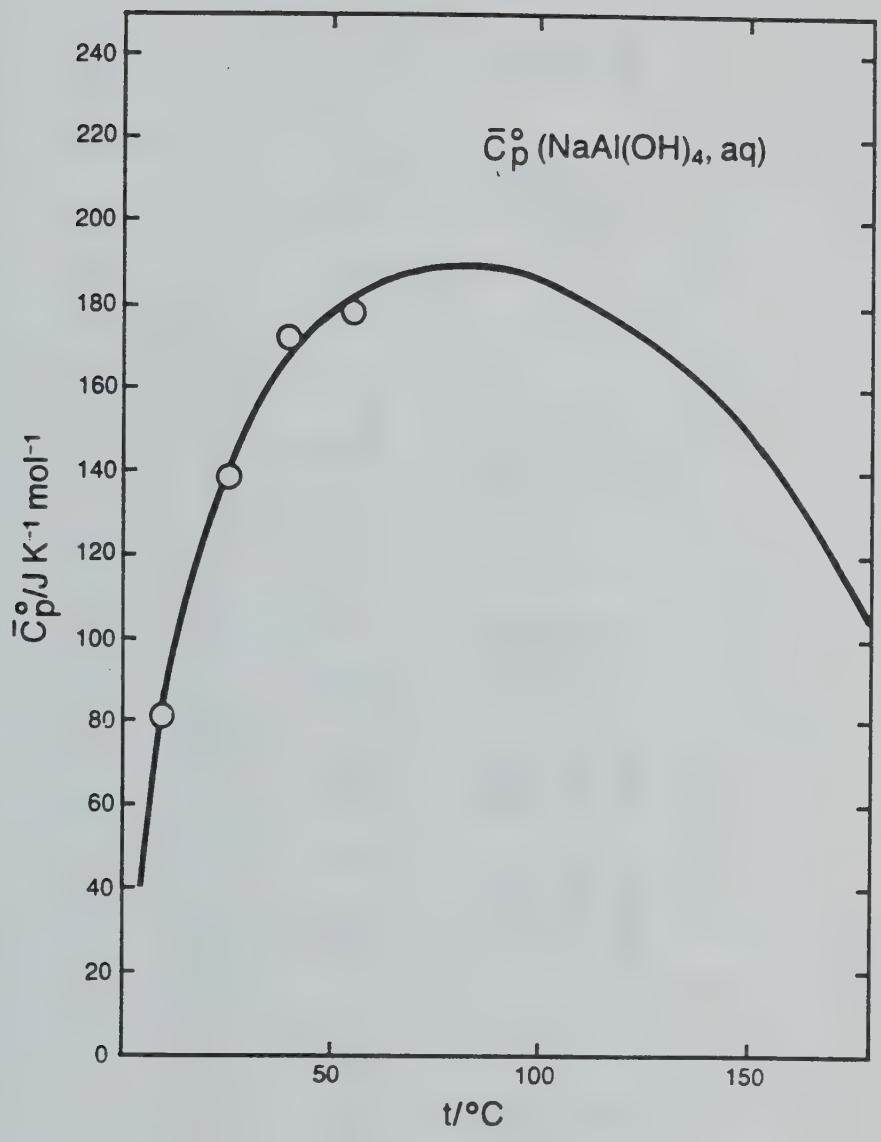

Figure 7.6: Standard state heat capacities for $NaAl(OH)_4(aq)$. The solid line is the extrapolation produced from a fit of the Helgeson-Kirkham-Flowers model to the 10-55°C data.

Table 7.8: Parameters from HKF model for selected species.

Species	σ ($cm^3 mol^{-1}$)	ξ ($cm^3 mol^{-1}$)	θ_V (K)	$10^{-5}\omega$ ($J\ mol^{-1}$)	c_1 ($J\ K^{-1} mol^{-1}$)	c_2 ($J\ K^{-1} mol^{-1}$)	θ_J (K)
$NaAl(OH)_4(aq)$	57.07	−1.2803	254	5.736	338.17	−21.38	254
$AlCl_3(aq)$	32.08	−0.9130	246	30.29	113.2	−56.91	246
$HCl(aq)$	23.39	−0.2446	259	6.093	14.22	−14.52	246
$NaCl(aq)$	30.84	−2.2945	228	7.475	111.43	−20.43	250

and HCl(aq) with the Gibbs free energy for NaCl(aq) taken from PITZER *et al.* (1984), and values for the elements taken from APPS *et al.* (in prep.) :

$$\Delta G^\circ_{f,T}[Al(OH)_4^-,\ aq] = \Delta G^\circ_T[NaAl(OH)_4,\ aq] - \Delta G^\circ_T(NaCl,\ aq) + \Delta G^\circ_T(HCl,\ aq) + \Delta G^\circ_T(\text{elements},\ 298.15 - T) \quad (7.45)$$

The results are summarized in Table 7.9.

These extrapolated Gibbs free energies of formation can be compared with those obtained from solubilities of aluminum oxide and hydroxides in alkaline solutions. Values from the critical compilations of APPS *et al.* (1986, in prep.) and CHANG (1982) are listed in Table 7.9 along with values calculated from the experimental results for the solubility of boehmite from KUYUNKO it et al. (1983). The values from CHANG (1982), which were originally referenced to the elements in their standard states at 25°C, were converted to conventional Gibbs free energies of formation using data for the elements from APPS *et al.* (in prep.). The differences between the Gibbs free energies for $Al(OH)_4^-(aq)$ extrapolated from our 10 to 55°C heat capacities and volumes and the critically evaluated results chosen by Apps *et al.* are shown in Figure 7.7. The agreement is excellent. The two sets of data differ by less than 1 kJ mol^{-1} to 200°C and by less than 3 kJ mol^{-1} at 300°C. This difference in the Gibbs free energy lies within estimates of the uncertainties by APPS *et al.* (1986, in prep.), that correspond to $\pm$ 0.25 in log K.

As an example, solubility products for boehmite calculated from both sets of free energies are plotted in Figure 7.8, along with the experimental data (KUYUNKO it et al., 1983; APPS, 1970; BERNSHTEIN and MASTSENOK, 1961; FULDA and GINSBERG, 1951; MAGARSHAK, 1938; DRUZHININA, 1955; RUSSELL *et al.*, 1955; WEFERS, 1967) compiled by APPS *et al.* (in prep.). The solubility reaction is

$$AlOOH(c) + H_2O(l) + OH^-(aq) = Al(OH)_4^-(aq) \quad (7.46)$$

The calculation is based on our values for ΔG°_f [$NaAl(OH)_4$, aq] and values for ΔG°_f (AlOOH, c) from APPS *et al.* (in prep.), ΔG°_f (H_2O, l) from HELGESON and KIRKHAM (1974), and ΔG°_w [$H_2O(l) = H^+(aq) + OH^-(aq)$] from BUSEY and MESMER (1978) according to the scheme:

$$\Delta G^\circ_T(\text{Rxn. 7.46}) = -RT \ln K$$

Table 7.9: Comparison of calculated and experimental values of ΔG_f° [$Al(OH)_4^-$, aq].

	ΔG_f°[$Al(OH)_4^-$, aq]/kJ mol^{-1} *				
t/°C	calc†	calc‡	APPS *et. al.* (in prep.)	KUYUNKO *et al.* (1983)	CHANG 1982
0	−1321.84	−1320.77	−1320.75	–	–
25	−1305.59	(−1304.83)	−1304.83	−1305.0	−1305.2
50	−1289.20	−1288.76	−1288.76	−1288.7	–
60	−1282.63	−1282.31	−1282.30	–	−1282.1
100	−1256.29	−1256.47	−1256.38	−1255.8	−1255.5
150	−1223.24	−1224.05	−1223.59	−1222.9	−1221.5
200	−1189.95	−1191.35	−1190.18	−1189.3	−1186.1
250	−1155.79	−1157.85	−1155.63	−1155.3	−1149.6
300	−1119.09	−1121.77	−1118.92	−1120.8	−1112.7
350			−1077.11	–	–

* Conventional standard state Gibbs free energies of formation from the elements at temperature t. Uncertainties are discussed in the text.

† Calculated using the values of $\Delta G_{f,298}^\circ$ and $\bar{S}_{298}^\circ$ for $Al(OH)_4^-$(aq) from this work.

‡ Calculated using the values of $\Delta G_{f,298}^\circ$ and $\bar{S}_{298}^\circ$ for $Al(OH)_4^-$(aq) from APPS *et al.* (in prep.).

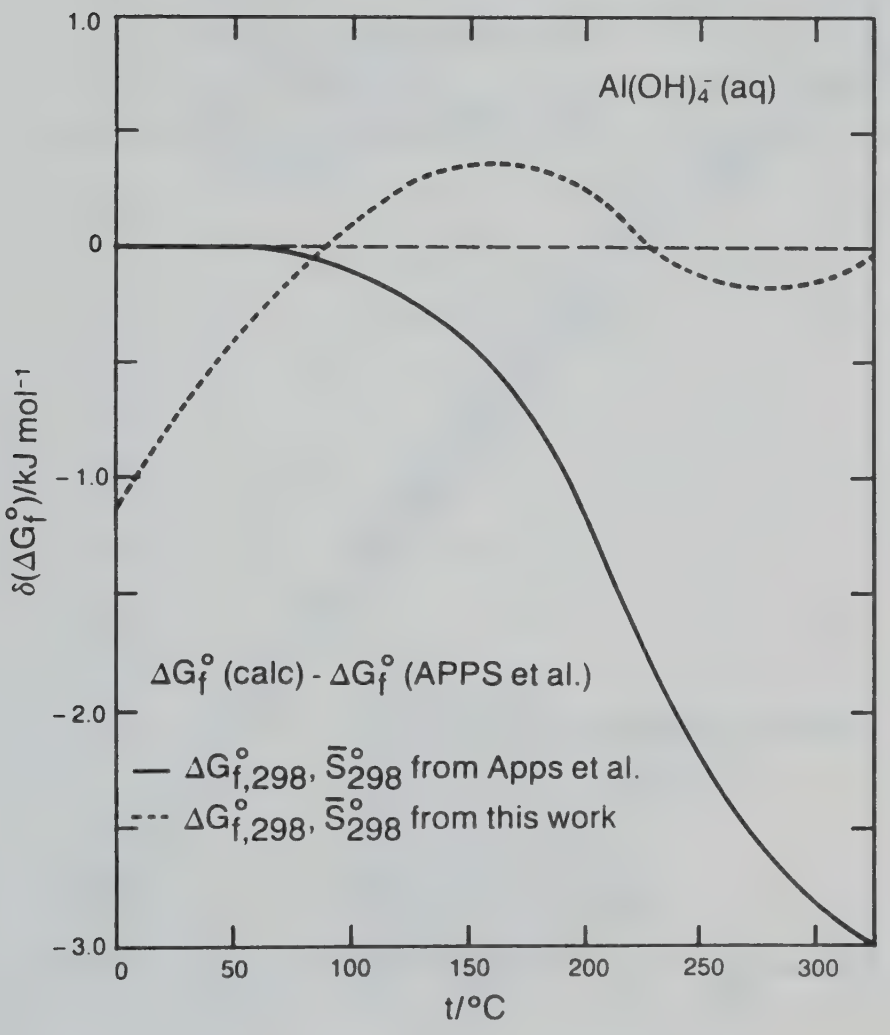

Figure 7.7: Deviation of the calculated Gibbs free energies of the aluminate ion $\delta(\Delta G_f^\circ) = \Delta G_f^\circ[\mathrm{Al(OH)_4^-}, \mathrm{aq\ (this\ work)}]$ - $\Delta G_f^\circ[\mathrm{Al(OH)_4^-}, \mathrm{aq\ (APPS}\ \textit{et al.}, \mathrm{in\ prep.})]$.

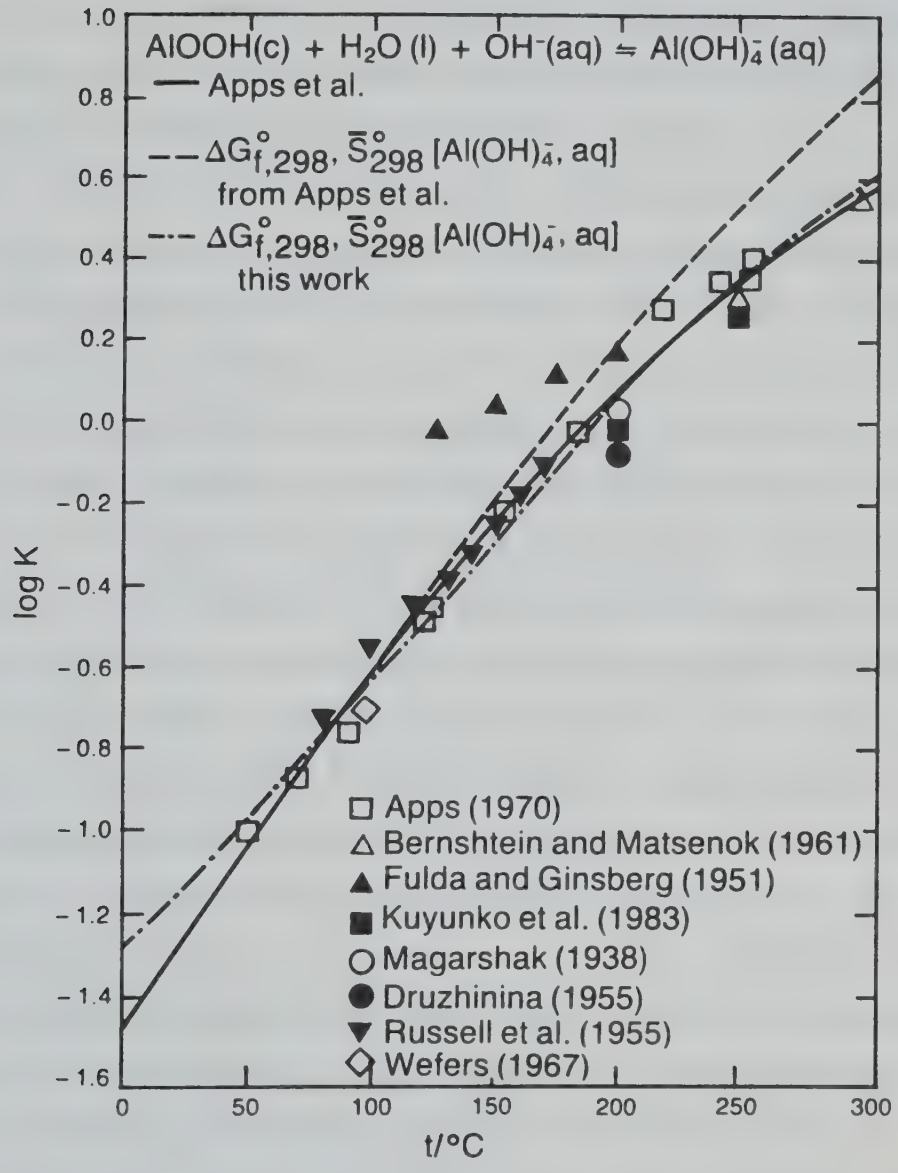

Figure 7.8: Comparison of boehmite solubility product constants as compiled by APPS *et al.* (in prep.) with values calculated from this work.

$$= \Delta G^{\circ}_{f,T}[\mathrm{NaAl(OH)_4,\ aq}] - \Delta G^{\circ}_{f,T}(\mathrm{NaCl,\ aq}) + \Delta G^{\circ}_{f,T}(\mathrm{HCl,\ aq})$$
$$-\Delta G^{\circ}_{f,T}(\mathrm{AlOOH,\ c}) - \Delta G^{\circ}_{w,T}[\mathrm{H_2O(l) = H^+(aq) + OH^-(aq)}]$$
$$-2\Delta G^{\circ}_{f,T}(\mathrm{H_2O,\ l}) \qquad (7.47)$$

The results in Figure 7.8 clearly illustrate that the extrapolation based on 10-55°C heat capacity and volume results yields calculated quantities that lie within the statistical scatter of careful direct measurements up to 200°C.

It is worth noting that the uncertainty in the value of the standard state entropy for $Al(OH)_4^-$(aq) accounts for all observed differences between the calculated solubility products for boehmite and those from direct solubility measurements. For example, the compilation by WAGMAN *et al.* (1982) cites a value $\bar{S}^{\circ}_{298}[Al(OH)_4^-, aq] =$ 102.9 J $K^{-1}mol^{-1}$, which differs from the preferred value of APPS *et al.* (in prep.) by almost 21 J $K^{-1}mol^{-1}$. Because of this uncertainty, calculations with our high temperature heat capacity function for $Al(OH)_4^-$(aq) derived from our fits with the HKF model, in association with results of direct solubility measurements on boehmite as given in Figure 7.8 have been made in the hope of obtaining improved room temperature thermodynamic values for the aqueous aluminate ion. The boehmite solubility data were used instead of the data for other aluminum minerals because of the precision of the boehmite data at moderately high temperatures (in the region from 100 to 200°C where our extrapolation is thought to be quite accurate). We have fitted all of the data shown in Figure 7.8 (APPS *et al.*, in prep.; KUYUNKO *et al.*, 1983; APPS, 1970; BERNSHTEIN and MASTSENOK, 1961; FULDA and GINSBERG, 1951; MAGARSHAK, 1938; DRUZHININA, 1955; RUSSELL *et al.*, 1955; WEFERS, 1967), excluding those of FULDA and GINSBERG (1951) that seem to be inconsistent with the other data. Data for the region below 200°C were weighted twice twice as heavily as data for temperatures above 200°C. Expressions of type (7.44) were fitted to the Gibbs free energies of $Al(OH)_4^-$(aq) derived from the solubility measurements using the auxiliary data previously mentioned, and the present heat capacity and volume functions. The only variable parameters were the standard state Gibbs free energy and the standard state entropy at 298 K. The fit resulted in revised values equal to $\Delta G^{\circ}_{f,298}$ = -1305.6 ± 0.2 kJ mol^{-1} and $\bar{S}^{\circ}_{298}$ = 111.3 ± 1 J $K^{-1}mol^{-1}$ for $Al(OH)_4^-$(aq), where the ± values are statistical estimates of the standard deviations. HEMINGWAY

et al. (1978) have selected $\Delta G^{\circ}_{f,298}[Al(OH)^{-}_{4}, aq]$ = -1305 ± 1 kJ mol^{-1}, and typical $\bar{S}^{\circ}_{298}$ $[Al(OH)^{-}_{4}, aq]$ values range from 102.9 (WAGMAN *et al.*, 1982) to 123.8 (APPS *et al.*, in prep.) J $K^{-1}mol^{-1}$. Both of these sets of data show that the results of our fits are within the currently placed uncertainties of thermodynamic values for $Al(OH)^{-}_{4}(aq)$. It is estimated that the total uncertainties in the presently reported values are ± 1 kJ mol^{-1} for $\Delta G^{\circ}_{f,298}$ and ± 10 J $K^{-1}mol^{-1}$ for $\bar{S}^{\circ}_{298}$. The Gibbs free energies for $Al(OH)^{-}_{4}(aq)$ from 0 to 300°C have been calculated using these revised values and are listed in Table 7.9. The curve associated with regression of the equation of type (7.44) to the direct solubility measurements of boehmite is shown along with others in Figure 7.8.

Data from the same sources cited previously and Tables 7.7 and 7.8 [except for the revised Gibbs free energy and entropy for $Al(OH)^{-}_{4}(aq)$ discussed above] have been used to calculate values of ΔG°_{T} for the hydrolysis reaction

$$Al^{3+}(aq) + 4OH^{-}(aq) = Al(OH)^{-}_{4}(aq) \tag{7.48}$$

based on the scheme

$$\begin{aligned}\Delta G^{\circ}_{T}(\text{Rxn. 7.48}) \;=\; & \Delta G^{\circ}_{f,T}[NaAl(OH)_4,\ aq] - \Delta G^{\circ}_{f,T}(NaCl,\ aq) + \\ & 4\Delta G^{\circ}_{f,T}(HCl,\ aq) - \Delta G^{\circ}_{f,T}(AlCl_3,\ aq) + 4\Delta G^{\circ}_{w,T}[H_2O(l) = \\ & H^{+}(aq) + OH^{-}(aq)] - 4\Delta G^{\circ}_{f,T}(H_2O,\ l)\end{aligned} \tag{7.49}$$

The results from this calculation are given in Table 7.10 for temperatures up to 300°C, along with experimental results based on the solubility measurements by KUYUNKO *et al.* (1983). The predicted and experimental Gibbs free energies agree to within 1.5 kJ mol^{-1} (1.1 kJ mol^{-1} is due to a different $\Delta G^{\circ}_{f,298}$) up to 100°C. At higher temperatures, $Al^{3+}(aq)$ becomes less stable relative to the hydrolyzed species, and values for $\Delta G^{\circ}_{f,T}$ (Al^{3+}, aq) cannot be obtained accurately from any of the solubility data reported to date. Values for $\Delta G^{\circ}_{f,T}$ (Al^{3+}, aq) derived from this calculation are also included in Table 7.10. It is believed that the extrapolated Gibbs energies for $Al^{3+}(aq)$ and $Al(OH)^{-}_{4}(aq)$ are the best values now available.

Table 7.10: Standard Gibbs free energies (kJ mol^{-1}) for $Al^{3+}(aq)$ and its hydrolysis to aluminate.

		$Al^{3+}(aq) + 4OH^-(aq) = Al(OH)_4^-(aq)$	
t/°C	$\Delta G_f^\circ(Al^{3+}, aq)$*	ΔG°(calc)	ΔG°(KUYUNKO *et al.*, 1983)
0	−497.2	−176.3	–
25	−489.4	−187.0	−185.9
50	−481.7	−199.2	−198.2
100	−466.8	−226.2	−227.6
150	−452.7	−255.9	–
200	−439.6	−288.7	–
250	−428.8	−324.7	–
300	−420.0	−363.1	–

* Conventional standard state Gibbs energies of formation from the elements at temperature t. The relative uncertainty in the standard state entropy of formation of $Al^{3+}(aq)$ is the largest source of error in these calculations. Uncertainties in these extrapolated values are estimated to be ± 3 kJ mol^{-1} at 300°C, decreasing to ± 1 kJ mol^{-1} at 25°C.

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Chapter 8

Thermodynamics of aqueous boron: Standard state heat capacities and volumes from 10 to 55°C of boric acid and sodium borate. Calculations of selected equilibria to high temperatures.

8.1 Introduction

Knowledge of the thermodynamic properties of aqueous boron species is important for a description of many equilibria such as those required to describe standard pH buffers, those present in ocean water at atmospheric and higher pressures (WARD and MILLERO, 1974; CULBERSON and PYTKOWICZ, 1968), at higher temperatures for dissolution reactions of boron-containing minerals (DEVINA *et al.*, 1982), and reactions associated with the poisoning of coolants in pressurized water nuclear reactors (MESMER *et al.*, 1972). There are numerous equilibrium studies at or near room temperature and also others at much higher temperatures (MESMER *et al.*, 1972).

The present experiments were undertaken in part to study many of the problems cited above, but also for other less applied reasons. The mononuclear aqueous boron species closely resemble several hydrolyzed aqueous species for many trivalent cations. Of present interest are the ions formed from the trivalent cations Fe^{3+} and Al^{3+}. Species such as $Al(OH)_3(aq)$ and $Fe(OH)_3(aq)$ are too insoluble for direct calorimetric measurements, whereas $B(OH)_3(aq)$ can be obtained to concentrations of almost one molal near room temperature. Many species resembling $Fe(OH)_4^-(aq)$ are also too insoluble for direct measurements, or require large amounts of hydroxide to maintain the ion in sufficient concentrations for experimental measurements [such as those described in Chapter 7 involving $Al(OH)_4^-(aq)$]. Since the thermodynamic properties of many hydrolyzed aqueous species are important for many of the reasons

described in the preludes to this Chapter and the preceding Chapter, measurements associated with boric acid and the borate ion can provide key data that can be used to help describe the thermodynamics of several insoluble metal hydroxides.

The structural evidence from a variety of spectroscopic studies suggests that $B(OH)_3(aq)$ and $B(OH)_4^-(aq)$ are probably isostructural with $Al(OH)_3(aq)$ and $Al(OH)_4^-(aq)$. $B(OH)_4^-(aq)$ has been shown by Raman and infrared spectroscopy (EDWARDS *et al.*, 1955) to be tetrahedral in solution. A similar structure has been proposed for $Al(OH)_4^-(aq)$, as discussed in the preceding chapter. It is also reasonable to assume that the trigonal planar structure (C_{3h}) deduced for $B(OH)_3(aq)$ (SERVOSS and CLARK, 1957) also applies to the structure of the inaccessible (low solubility) $Al(OH)_3(aq)$ species.

Partial molar volumes and heat capacities are useful in describing the pressure and temperature dependence of chemical equilibria. The relationships of the equilibrium constant for a reaction to partial molar volumes and heat capacities can be seen in the following equations:

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \tag{8.1}$$

$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_p = \Delta C_p^\circ \tag{8.2}$$

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta V^\circ}{RT} \tag{8.3}$$

It was for the reasons cited above that the densities and heat capacities of aqueous solutions containing $B(OH)_3$ and $NaB(OH)_4$ were measured from 10 to 55°C. These results lead to calculations of the corresponding partial molar properties that are used in classical calculations of boric acid equilibria and to less classical applications as discussed in Chapter 10.

8.2 Experimental

Water used for all experiments was first passed through an activated charcoal filter, then through a Milli-RO4/Milli-Q reagent grade mixed bed ion exchange column and activated carbon system to achieve a final resistivity of 18 MΩ cm or greater. NaOH

solutions were prepared from Fisher (certified, ACS) carbonate-free 50% solutions and standardized by titration against potassium hydrogen phthalate. Boric acid and sodium borate solutions were prepared from Fisher (certified, ACS) boric acid.

One stock solution was prepared by adding boric acid powder to water, and another was prepared by adding boric acid to a solution containing a known amount of NaOH sufficient to ensure that all of the boric acid would be converted to sodium borate. Boric acid in the first stock solution was determined by titration using mannitol as described by VOGEL (1978). Hydroxide and borate concentrations were determined for the second solution by two titrations, the first with acid, and the second with base and mannitol (VOGEL, 1978). More dilute solutions were prepared by mass with water as the diluent for the stock solution containing boric acid, and with dilute (0.1 molal) NaOH as the diluent for the stock solution containing sodium borate. All solutions were stored under nitrogen in the presence of CO_2-scavenging dessicants (Ascarite and NaOH pellets). All handling of solutions was done with minimum exposure to air.

Heat capacities and volumes were measured relative to water with a Sodev model CP-C Picker flow microcalorimeter (PICKER *et al.*, 1971) and Sodev model 03D densimeter (PICKER *et al.*, 1974). The temperature of both instruments was controlled to $\pm$ 0.001°C with independent Sodev CT-L circulating baths. The temperature was monitored with thermistors that had been calibrated with a Hewlett Packard 2804A quartz thermometer and placed just upstream of the measuring cells.

The densimeter and calorimeter were calibrated with a standard 1 m NaCl solution using density and heat capacity data from MILLERO (1970) and DESNOYERS *et al.* (1976), respectively. The calorimetric measurements were corrected for a very small heat leak by the method of DESNOYERS *et al.* (1976) as described in Chapter 2. The correction factor was found to be $f = 1.006 \pm 0.001$ at 25°C and was assumed to be independent of temperature (TREMAINE *et al.*, 1986). The densities and specific heat capacities of water at 10, 25, 40 and 55°C were taken from KELL (1967, 1972) (and are listed in Chapter 4, Table 4.2).

8.3 Results

8.3.1 Apparent Molar Properties

Boric acid

The experimentally determined relative densities $(d - d_1^\circ)$ and heat capacity-density ratios $\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$ for solutions containing $B(OH)_3$ are listed in Table 8.1.

Apparent molar properties $({}^\phi Y)$ of single solutes that are dissolved in some solvent are defined by

$$ {}^\phi Y = \frac{Y_{sol} - 55.509 Y_1^\circ}{m} \tag{8.4} $$

where Y_{sol} is the extensive property (heat capacity or volume) of an amount of solution containing one kilogram of water, Y_1° is the molar heat capacity or volume of water, and m is the molality of the solute. Apparent molar volumes and heat capacities were calculated from the density and heat capacity results listed in Table 8.1 by the following equations:

$$ {}^\phi V = \frac{\frac{1 + mM}{d} - \frac{1}{d_1^\circ}}{m} \tag{8.5} $$

and

$$ {}^\phi C_p = \frac{c_p(1 + mM) - c_{p,1}^\circ}{m} \tag{8.6} $$

Here M is the solute molecular weight, c_p and d are the specific heat capacity and density of the solution, and $c_{p,1}^\circ$ and d_1° are the specific heat capacity and density of water, respectively.

The equations used to fit apparent molar properties of electrolytes, as discussed in detail in Chapter 2 and Chapter 4, are all based on the Debye-Hückel theory that allows for the long range electrostatic interactions between ions that are the principal source of non-ideal properties of dilute solutions of such charged species. For non-electrolytes there are no long range interactions due to ionic charges, which means that equations of the Debye-Hückel type are irrelevant and terms in $m^{1/2}$ need not be considered. Instead, useful equations of the form

$$ {}^\phi Y = \bar{Y}^\circ + B_Y I \tag{8.7} $$

Table 8.1: Compositions of solutions and experimental apparent molar volumes and heat capacities for aqueous solutions containing $B(OH)_3$.

m (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	$^\phi V$ (cm^{3}mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	$^\phi C_p$ (J K^{-1}mol^{-1})
		10°C		
0.4799	1.0788	38.94	−0.8562	86.1
0.4029	0.9114	38.86	−0.7297	84.9
0.2916	0.6615	38.89	−0.5351	84.3
0.1985	0.4521	38.89	−0.3704	83.3
0.09316	0.2126	38.93	−0.1766	82.6
		25°C		
0.7903	1.6589	40.23	−1.009	112.2
0.6008	1.2717	40.21	−0.7895	110.9
0.4799	1.0223	40.18	−0.6422	110.0
0.4029	0.8612	40.16	−0.5407	109.9
0.2916	0.6261	40.16	−0.3974	109.3
0.1985	0.4276	40.18	−0.2737	108.9
0.09316	0.2016	40.17	−0.1312	107.8
		40°C		
0.7903	1.5924	41.19	−0.8296	125.2
0.6008	1.2200	41.19	−0.6461	124.4
0.4799	0.9808	41.15	−0.5222	123.9
0.4029	0.8248	41.18	−0.4446	123.5
0.2916	0.6010	41.13	−0.3255	123.0
0.1985	0.4109	41.12	−0.2241	122.9
0.09316	0.1942	41.06	−0.109	120.4
		55°C		
0.7903	1.5434	41.97	−0.7077	133.9
0.6008	1.1876	41.88	−0.5584	132.6
0.4799	0.9544	41.86	−0.4438	132.7
0.4029	0.8020	41.90	−0.3755	132.7
0.2916	0.5838	41.87	−0.2722	132.7
0.1985	0.3971	41.97	−0.1866	133.0
0.09316	0.1865	42.04	−0.0876	133.4

can be used for extrapolation of results to infinite dilution and as anytical representations of many experimental results. In this equation $\bar{Y}^\circ$ is the value of the apparent molar property at infinite dilution (equal to the partial molar property), and B_Y is an adjustable parameter that is related to molecular interactions.

Apparent molar volumes and heat capacities for boric acid that are listed in Table 8.1 were fitted by the ${}^\phi C_p$ and ${}^\phi V$ versions of eq. 8.7. Results of these fits are listed in Tables 8.3 and 8.4 along with the fits to the data for the sodium borate solutions described below. The values of the B_Y parameters obtained from 10 to 55°C were found to be well represented by linear equations of the form

$$B_Y = p_1 + p_2 T \tag{8.8}$$

in which the p_i coefficients are adjustable parameters and T is the temperature in Kelvins. No meaningful differences in the limiting standard state properties were observed after refitting the data in Table 8.1 to B_Y values constrained to eq. 8.8. Tables 8.3 and 8.4 list all of these values along with statistical estimates of the uncertainties from fits with unconstrained B_Y parameters. Figures 8.1 and 8.2 show plots of the apparent molar volumes and heat capacities of $B(OH)_3$ versus molality that illustrate the good quality of the fits.

Sodium borate and sodium hydroxide mixtures

The experimentally determined relative densities $(d - d_1^\circ)$ and heat capacity density ratios $\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$ for solutions containing $NaB(OH)_4$+NaOH are listed in Table 8.2. The notation used in Table 8.2 and elsewhere in this chapter follows the scheme (1 = H_2O, 2 = $NaB(OH)_4$, and 3 = NaOH).

The "experimental" apparent molar property ${}^\phi Y^{exp}$ of a solution is defined in terms of measured quantities as

$${}^\phi Y^{exp} = \frac{Y_{sol} - 55.509 Y_1^\circ}{m_2 + m_3} \tag{8.9}$$

where Y_{sol} and Y_1°, were defined previously and m_2 and m_3 are molalities of sodium borate and sodium hydroxide, respectively. Experimental apparent molar volumes and heat capacities were calculated from the results given in Table 8.2 by

$${}^\phi V^{exp} = \frac{\frac{1 + m_2 M_2 + m_3 M_3}{d} - \frac{1}{d_1^\circ} H}{m_2 + m_3} \tag{8.10}$$

Table 8.2: Compositions of Solutions and Experimental Apparent Molar Volumes and Heat Capacities for $NaB(OH)_4/NaOH$ mixtures.

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	ϕV^{exp} (cm^{3}mol^{-1})	$10^3\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	ϕC_p^{exp} (J K^{-1}mol^{-1})
			10°C		
1.1966	0.1108	9.0641	24.982	6.395	126.03
0.9721	0.1089	7.5811	23.662	0.864	102.62
0.7576	0.1071	6.1145	22.096	−3.353	75.91
0.5519	0.1053	4.6587	20.091	−6.088	44.55
0.3687	0.1038	3.3143	17.507	−7.191	8.55
0.2912	0.1031	2.7350	15.846	−7.016	−9.22
0.1897	0.1023	1.9602	12.771	−6.353	−38.73
0.1064	0.1015	1.3134	8.347	−5.228	−71.41
			25°C		
1.1966	0.1108	8.7013	27.525	13.60	160.06
0.9721	0.1089	7.2662	26.347	8.086	142.18
0.7576	0.1071	5.8478	24.960	3.634	122.09
0.5519	0.1053	4.4481	23.086	0.246	97.80
0.3687	0.1038	3.1624	20.509	−1.692	70.24
0.2912	0.1031	2.6066	18.920	−2.204	55.12
0.1897	0.1023	1.8681	15.754	−2.462	29.98
0.1064	0.1015	1.2492	11.278	−2.308	15.16
			40°C		
1.1966	0.1108	8.4322	29.342	17.77	181.06
0.9721	0.1089	7.0356	28.238	12.15	165.83
0.7576	0.1071	5.6590	26.903	7.629	149.53
0.5519	0.1053	4.3031	25.055	3.875	129.10
0.3687	0.1038	3.0563	22.543	1.310	105.25
0.2912	0.1031	2.5163	20.978	0.478	92.12
0.1897	0.1023	1.8023	17.780	−0.354	68.58
0.1064	0.1015	1.2070	13.081	−0.777	38.46

Table 8.2: (continued)

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	$^{\phi}V^{exp}$ (cm^{3}mol^{-1})	$10^3\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	$^{\phi}C_p^{exp}$ (J K^{-1}mol^{-1})
			55°C		
1.1966	0.1108	8.2622	30.400	20.86	195.18
0.9721	0.1089	6.9017	29.229	15.26	181.84
0.7576	0.1071	5.5528	27.876	10.34	166.52
0.5519	0.1053	4.2168	26.106	6.323	148.84
0.3687	0.1038	2.9937	23.599	3.267	126.74
0.2912	0.1031	2.4665	21.970	2.148	113.72
0.1897	0.1023	1.7634	18.838	0.951	91.45
0.1064	0.1015	1.1833	13.941	0.130	60.12

and

$$^{\phi}C_p^{exp} = \frac{c_p(1 + m_2M_2 + m_3M_3) - c^{\circ}_{p,1}}{m_2 + m_3} \tag{8.11}$$

where all symbols have been defined previously.

The sodium hydroxide was present in the solutions containing sodium borate to prevent hydrolysis, and must be accounted for in order to obtain the properties of sodium borate that is of interest here. Because of the success in using Young's rule to evaluate the properties of sodium aluminate from aluminate+hydroxide mixtures as described in Chapter 7, Young's rule was used here to account for the effects of sodium hydroxide on the measured total properties.

As stated in Chapter 7, Young's rule (YOUNG and SMITH, 1954) is an expression relating "experimental" apparent molar properties to apparent molar properties of pure components that make up a solution at the same total ionic strength of that solution. Young's rule is written as

$$^{\phi}Y^{exp} = \frac{m_2}{m_2 + m_3}{}^{\phi}Y_2 + \frac{m_3}{m_2 + m_3}{}^{\phi}Y_3 + \delta_{23}^{Y} \tag{8.12}$$

Here δ_{23}^{Y} is an excess mixing term that for 1:1 electrolytes has the form

$$\delta_{23}^{Y} = k_{23}\frac{m_2m_3}{(m_2 + m_3)^2}I \tag{8.13}$$

Several earlier investigations (MILLERO, 1979; REILLY and WOOD, 1969; Chapter 7) have provided evidence that the excess mixing term represented by eq. 8.13 makes a negligible contribution to $^{\phi}Y^{exp}$ for some 1:1 electrolyte mixtures, especially when the electrolytes have a common ion (Na^+ in these solutions) and when the molality of the electrolyte of particular interest is much larger than the molality of the other electrolyte. This last condition is met for all but the most dilute of the present solutions.

As discussed in detail in Chapter 4, $^{\phi}Y_2$ can be represented in terms of ionic strength by Debye-Hückel equations (MILLERO, 1979; PITZER and BREWER, 1961) of the form

$$^{\phi}Y_2 = \bar{Y}_2^{\circ} + \omega A_Y(\frac{3}{2})\left(\frac{1}{\Lambda} - \frac{\sigma}{3}\right)I^{1/2} + B_YI + C_YI^{3/2} \tag{8.14}$$

where

$$I = \omega m = \frac{1}{2}\sum m_iz_i^2 \tag{8.15}$$

$$\Lambda = 1 + I^{1/2} \tag{8.16}$$

$$\sigma = \frac{3\left(\Lambda - \frac{1}{\Lambda} - 2\ln\Lambda\right)}{I^{3/2}} \tag{8.17}$$

Values of the Debye-Hückel limiting slopes for apparent molar properties, A_Y (BRADLEY and PITZER, 1979), were taken from ANANTHASWAMY and ATKINSON (1984), and are listed in Chapter 4, Table 4.2.

Parameters for ${}^{\phi}Y_3$(NaOH) were obtained by fitting the Guggenheim equation to NaOH data from 0 to 3 m (ROUX *et al.*, 1984) as described in Chapter 7. The results of these fits are summarized in Chapter 7, Table 7.2.

Least squares fits of the data presented in Table 8.2 with equations 8.12 and 8.14 to 8.17 have led to values for the parameters $\bar{Y}_2^{\circ}$, $B_{Y,2}$ and $C_{Y,2}$. Fits with or without the interaction coefficient k_{23}^{Y} made no difference in the limiting standard state properties since the value of k_{23}^{Y} at 25°C was found to be equal to zero within derived statistical uncertainties. On the basis of these calculations, k_{23} was taken to be zero at all temperatures as for the data for aluminate solutions in the preceding Chapter. The values of the parameters B_Y and C_Y from least squares fits were represented by polynomials of the form

$$B_Y(\text{ and } C_Y) = p_1 + p_2T + p_3T^2 \tag{8.18}$$

without any significant loss in the accuracy of the fit to the experimental apparent molar properties. These constrained values of the B and C parameters were used in refitting the same equations to the experimental data. The infinite dilution properties that resulted from these constrained fits were found to be equal to those from unconstrained fits within the estimates of statistical uncertainties. Tables 8.3 and 8.4 list all of the fitted values for $\bar{Y}_2^{\circ}$, $B_{Y,2}$ and $C_{Y,2}$ along with associated statistical uncertainties from fits with unconstrained B_Y and C_Y terms. All of the expressions that were used to constrain the B_Y and C_Y parameters are given as footnotes to these tables.

Graphs of the apparent molar properties of $NaB(OH)_4$ minus the Debye-Hückel limiting slopes (given by eq. 8.14) against total ionic strength are given in Figures 8.3 and 8.4. The desired "goodness" of fit and precision of these experimental data can be seen in these Figures.

Table 8.3: Standard state partial molar volumes and concentration dependent parameters for $B(OH)_3$ and $NaB(OH)_4$.*†

t (°C)	$\bar{V}^\circ$ ($cm^3 mol^{-1}$)	B_V ($cm^3 kg\ mol^{-2}$)	C_V ($cm^3 kg^{3/2} mol^{-5/2}$)
	$B(OH)_3$		
10	38.89 ± 0.02	0.0467 ± 0.03	
25	40.15 ± 0.01	0.0907 ± 0.03	
40	41.09 ± 0.02	0.1348 ± 0.03	
55	41.86 ± 0.05	0.1788 ± 0.12	
		$NaB(OH)_4$	
10	20.32 ± 0.06	7.776 ± 0.3	-2.620 ± 0.2
25	24.32 ± 0.07	5.560 ± 0.3	-1.701 ± 0.3
40	26.94 ± 0.08	4.314 ± 0.2	-1.191 ± 0.2
55	28.02 ± 0.18	4.036 ± 0.9	-1.199 ± 0.7

* The uncertainties listed here correspond to statistical estimates of the standard deviations of each of the parameters from the unconstrained fits.

For $B(OH)_3$:

† $B_V = -0.7843 + 0.02935T$

For $NaB(OH)_4$:

† $B_V = 231.40 - 1.3995T + 0.0021535T^2$

$C_V = -96.41 + 0.58769T - 0.00090567T^2$

Table 8.4: Standard state partial molar heat capacities and concentration dependent parameters for $B(OH)_3$ and $NaB(OH)_4$.*†

t (°C)	${}^{\phi}C^{\circ}_{p,2}$ ($JK^{-1}mol^{-1}$)	B_J ($Jkg^{1/2}K^{-1}mol^{-3/2}$)	C_J ($J\ kg\ K^{-1}mol^{-2}$)
		$B(OH)_3$	
10	81.7 ± 0.3	8.552 ± 0.8	
25	107.4 ± 0.2	6.061 ± 0.4	
40	121.8 ± 0.5	3.569 ± 1.1	
55	132.6 ± 0.4	1.078 ± 0.9	
		$NaB(OH)_4$	
10	-64.5 ± 1.0	285.3 ± 5.0	-122.4 ± 3.9
25	31.8 ± 0.4	175.1 ± 2.2	-69.43 ± 1.7
40	87.9 ± 0.5	110.7 ± 2.3	-38.63 ± 1.8
55	119.5 ± 0.7	77.20 ± 3.6	-22.74 ± 2.8

* The uncertainties listed here correspond to statistical estimates of the standard deviations of each of the parameters from the unconstrained fits.

For $B(OH)_3$: $B_J = 55.583 - 0.16610T$

For $NaB(OH)_4$:

$B_J = -2534.9 + 5.1784T + \frac{126110}{T-190}$

$C_J = 1248.4 - 2.5277T - \frac{61019}{T-190}$

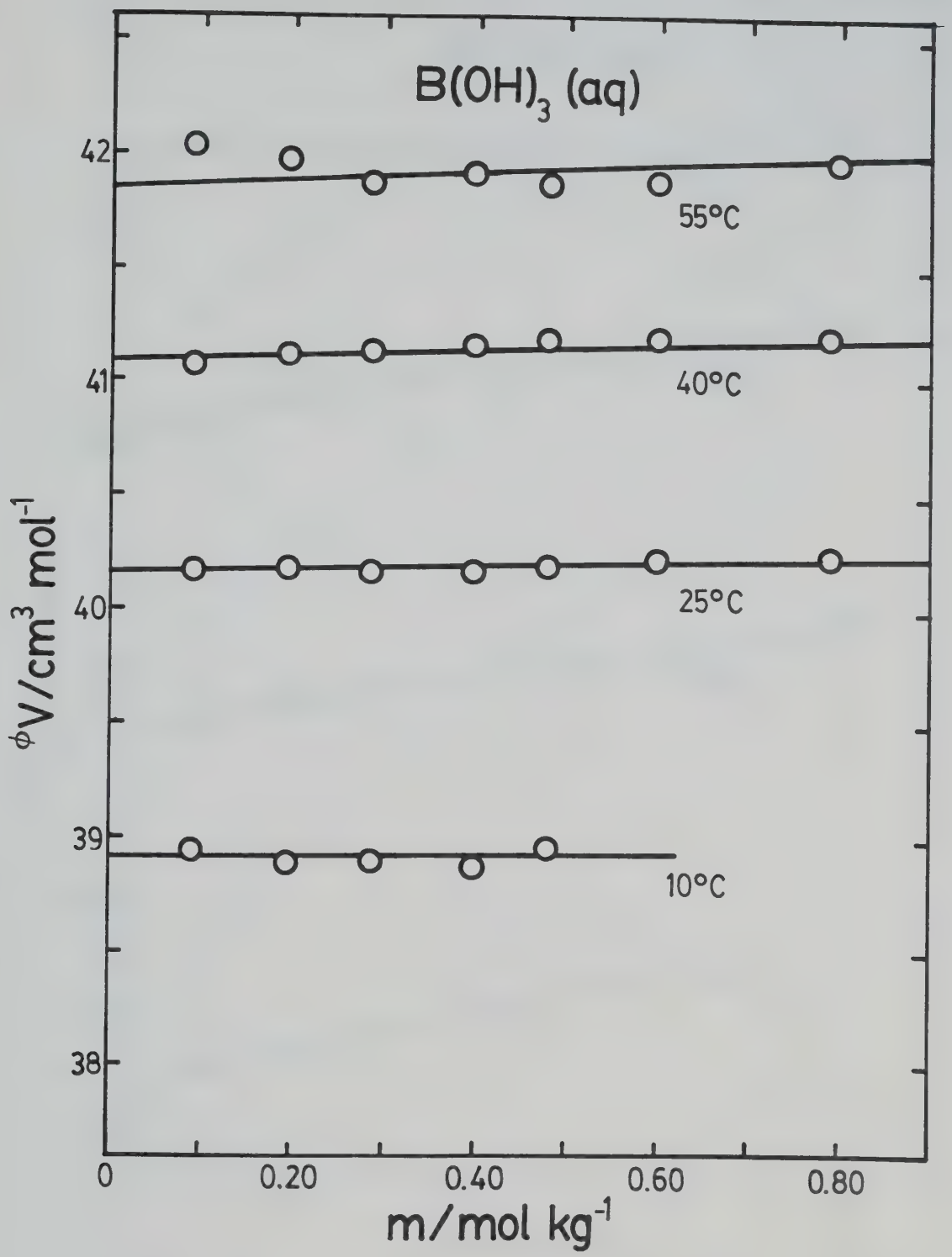
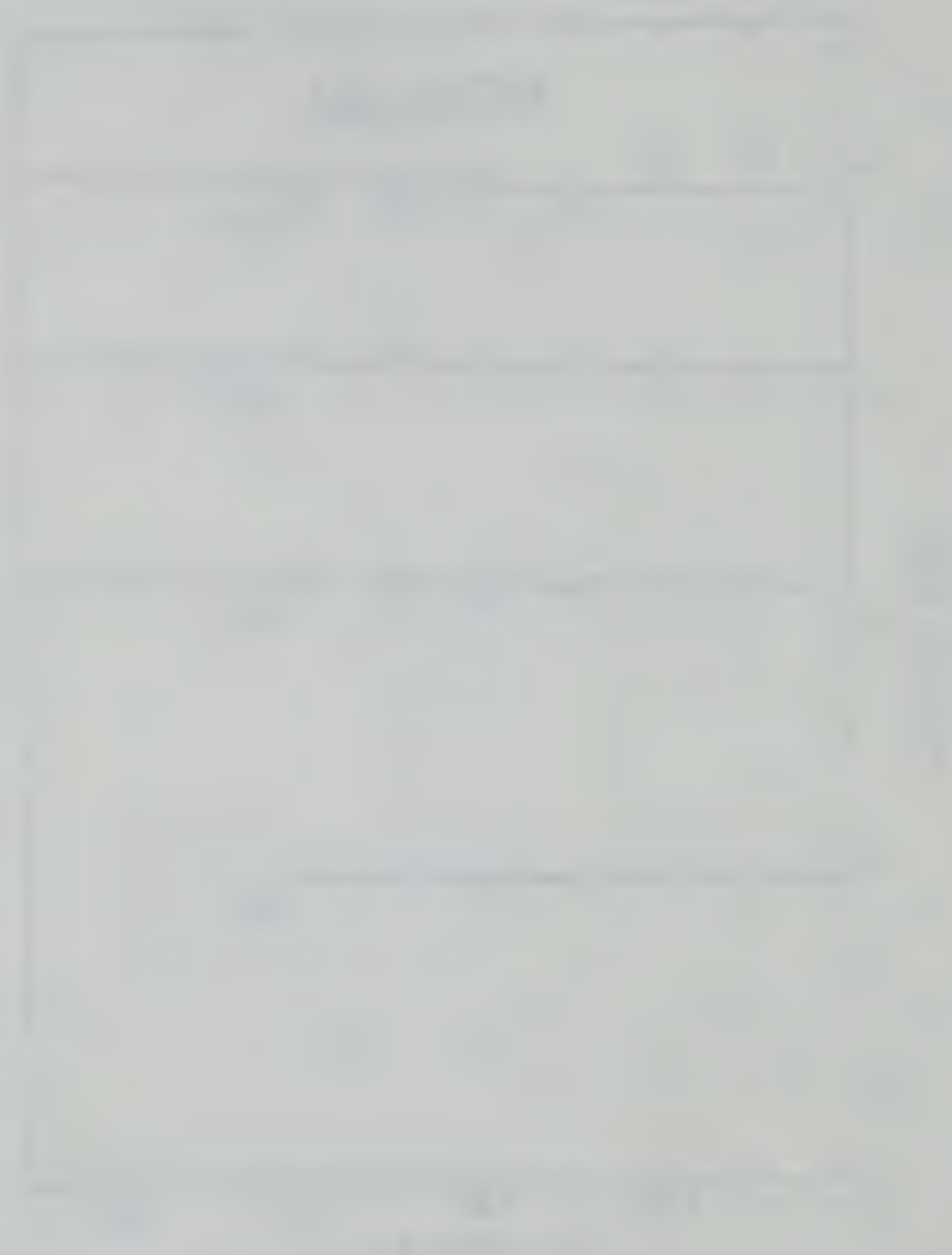


Figure 8.1: Apparent molar volumes and fitted equations (eq. 8.7) for $B(OH)_3$ from 10 to 55°C.



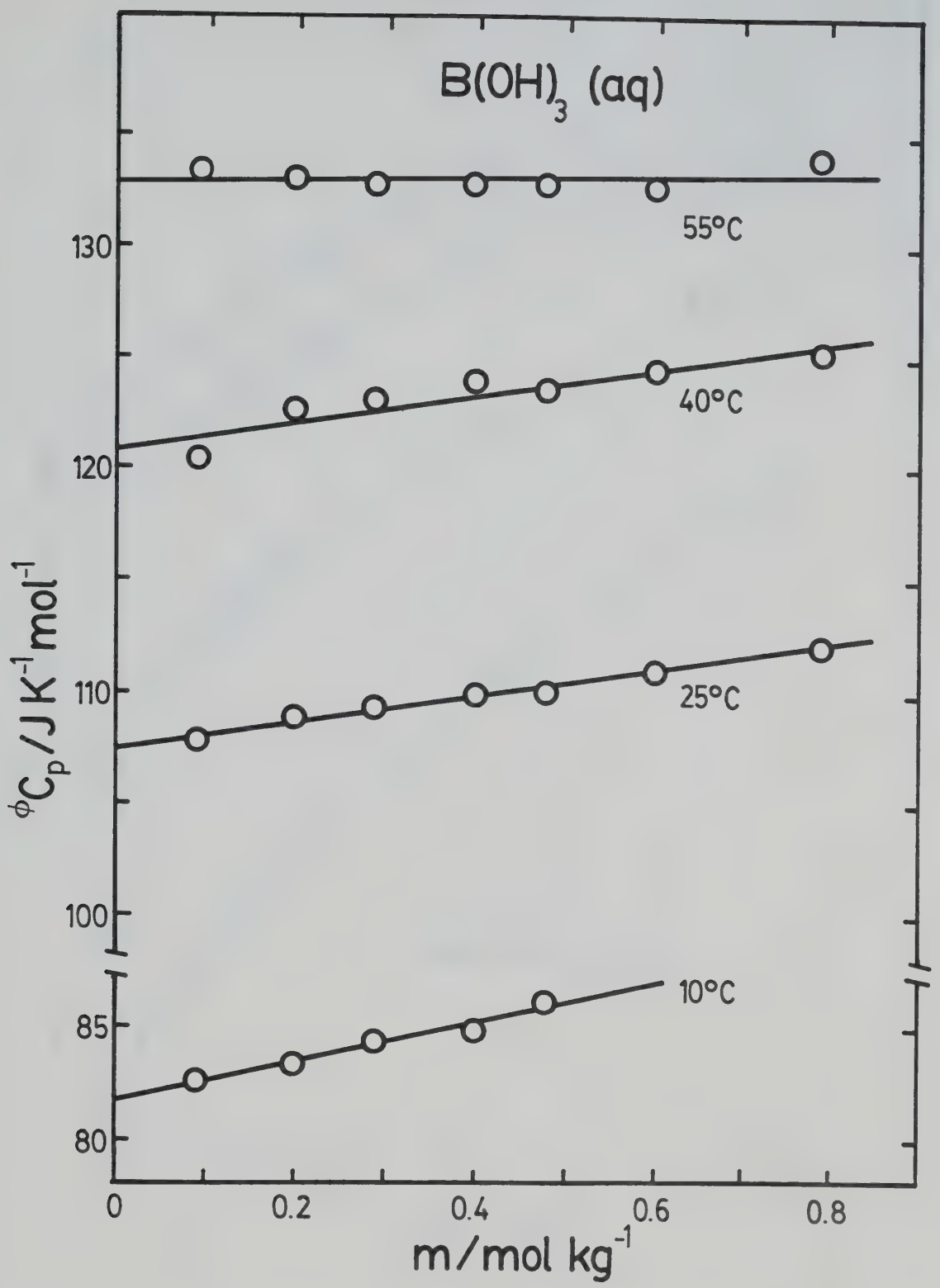


Figure 8.2: Apparent molar heat capacities and fitted equations (eq. 8.7) for $B(OH)_3$ from 10 to 55°C.

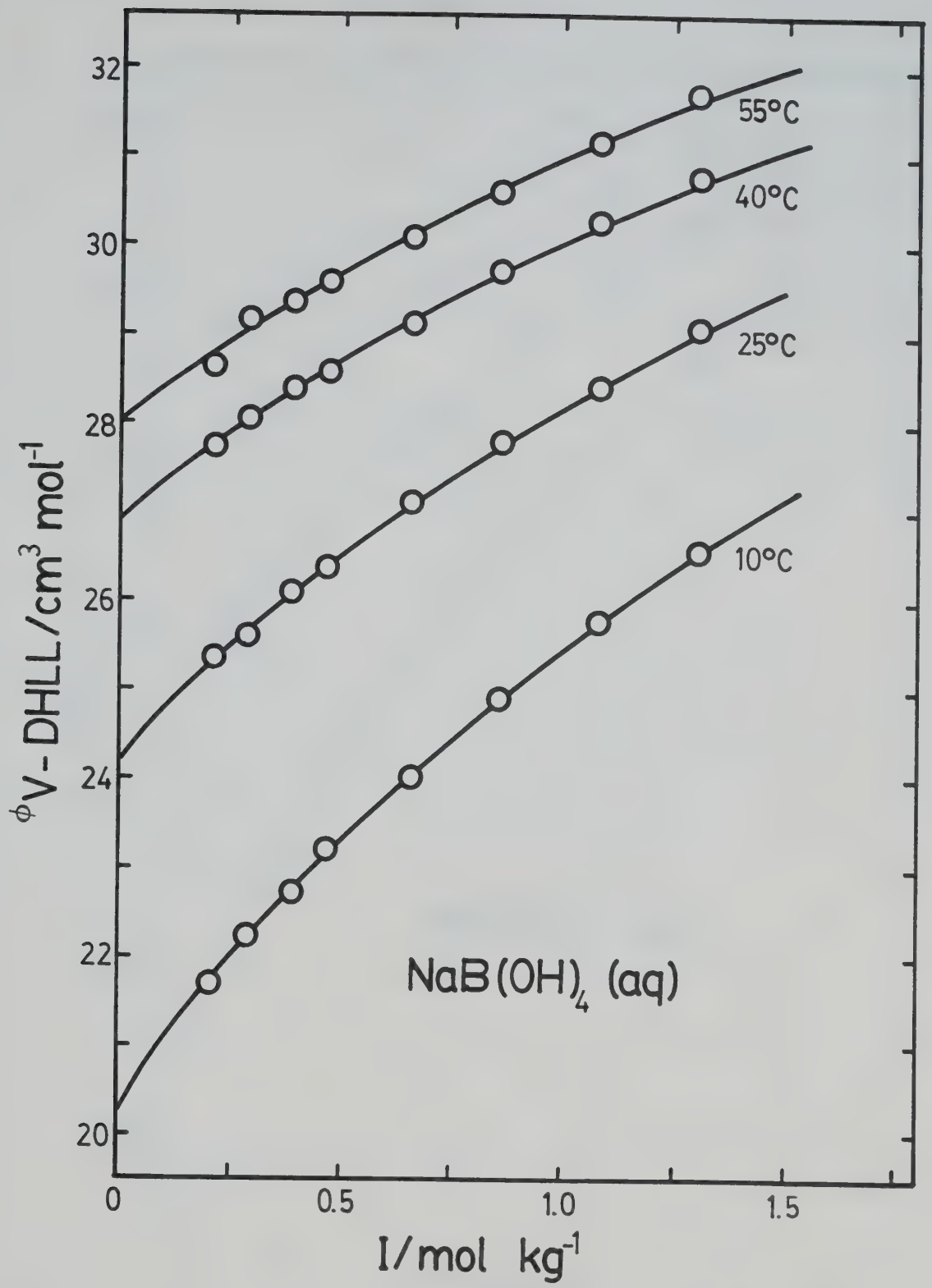


Figure 8.3: Apparent molar volumes of $NaB(OH)_4(aq)$ from 10 to 55°C derived from Young's rule after subtraction of the Debye-Hückel limiting law (DHLL) as given by eq. 8.14.

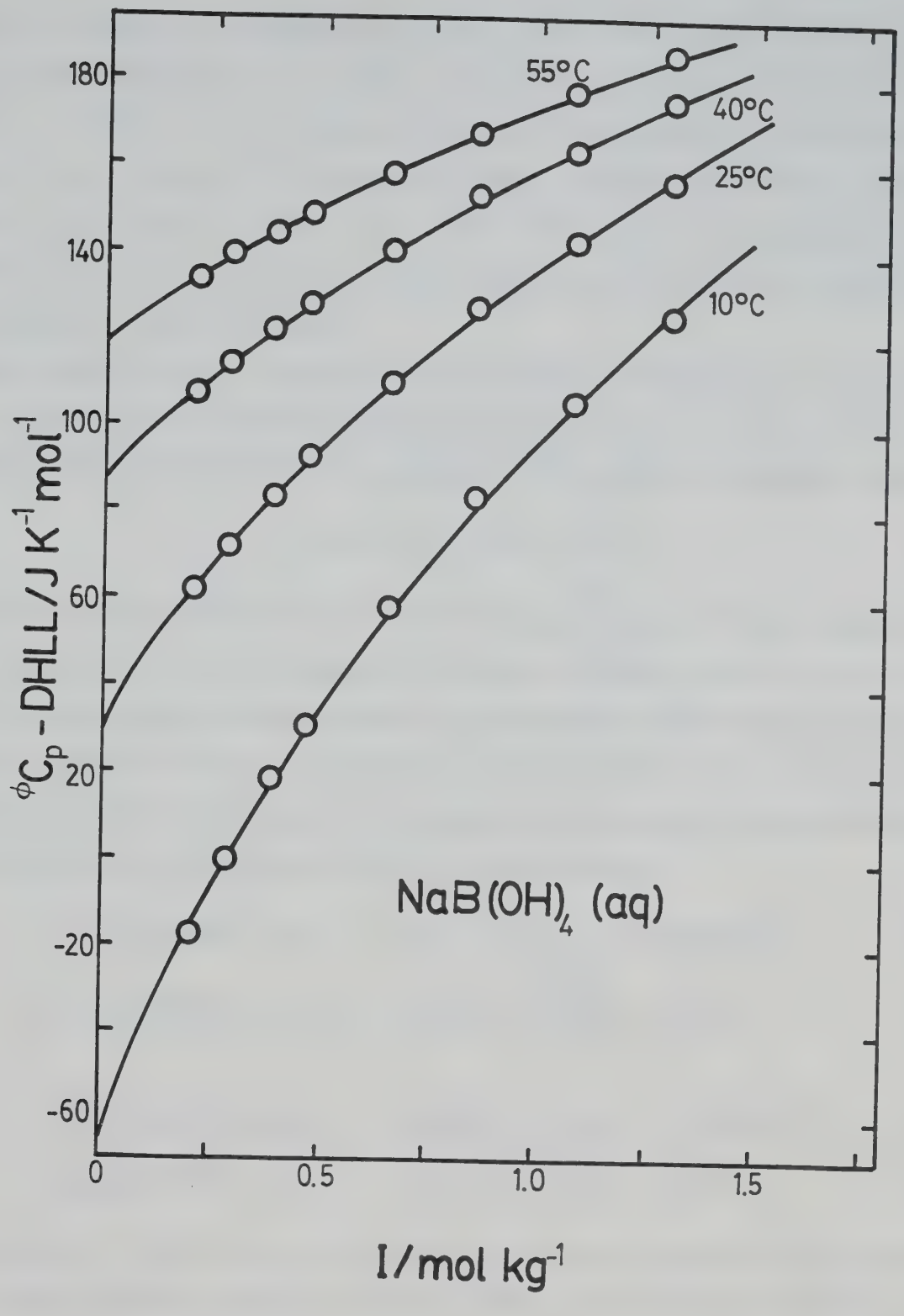


Figure 8.4: Apparent molar heat capacities of $NaB(OH)_4(aq)$ from 10 to 55°C derived from Young's rule after subtraction of the Debye-Hückel limiting law (DHLL) as given by eq. 8.14.

8.3.2 Standard State Properties

As mentioned earlier, the borate ion, $B(OH)_4^-$, has been shown to have a tetrahedral structure (EDWARDS *et al.*, 1955). Interactions of borate with Na^+ and other ions may be similar to such interactions by OH^- as discussed in reference to the aluminate ion in Chapter 7. One study, however, suggests that $B(OH)_4^-(aq)$ forms ion-pairs with $Na^+(aq)$ (CORTI *et al.*, 1980). The effects of ion pair formation (if proposed equilibrium constants are exactly right) are expected to be negligible upon extrapolations to infinite dilution.

The equation used to represent the temperature dependence of the standard state properties derived from the fitting procedures for the two solutes $B(OH)_3$ and $NaB(OH)_4$ described above is that suggested by HOLMES and MESMER (1983):

$$\bar{Y}_2^\circ = a + \frac{b}{T-\theta} + cT + dT^2 \tag{8.19}$$

It has proven useful (Chapters 4, 6, and 7; TREMAINE *et al.*, 1986) to constrain the θ parameter equal to 190 K as opposed to fitting it directly. We have fixed θ at 190 K, and have done least squares analyses on the limiting standard state properties in Tables 8.3 and 8.4 to generate appropriate parameters for eq. 8.19. The expressions that were derived for the temperature dependence of the standard state volumes and heat capacities for $B(OH)_3$ and $NaB(OH)_4$ are as follows:

$$\bar{V}_2^\circ[B(OH)_3,\ aq] = 48.63 - \frac{838.5}{T-190} - 0.0025489T \tag{8.20}$$

$$\bar{C}_{p,2}^\circ[B(OH)_3,\ aq] = 601.32 - \frac{25522}{T-190} - 0.86652T \tag{8.21}$$

$$\bar{V}_2^\circ[NaB(OH)_4,\ aq] = -328.32 + 2.1456T - 0.0032292T^2 \tag{8.22}$$

$$\bar{C}_{p,2}^\circ[NaB(OH)_4,\ aq] = 2298.3 - \frac{107460}{T-190} - 4.2699T \tag{8.23}$$

The equation for $\bar{V}_2^\circ[B(OH)_3,\ aq]$ is based on the present results over the temperature range 10-55°C and the results from ELLIS (1966) over the range 25 to 200°C, while each of the other three equations above is based only on the present results.

It is worthwhile to obtain expressions for the temperature dependence of the standard state properties of the anion $B(OH)_4^-(aq)$. For this purpose, standard state heat capacity and volume expressions for HCl(aq) and NaCl(aq) must be combined

with the present results for $NaB(OH)_4(aq)$ that are valid over the same temperature range. The expression that was reported in Chapter 7 for the standard state volumes of HCl(aq) [data used to derive this fit were taken from HERRINGTON *et al.* (1985) and ALLRED and WOOLLEY (1981)] and the expression for the standard state heat capacities of HCl(aq) [reported by TREMAINE *et al.* (1986)] were used. Expressions for the volume and heat capacity of NaCl(aq) were obtained from fits to the very precise data of MILLERO (1970), PERRON *et al.* (1975) and DESNOYERS *et al.* (1976). Other expressions for these properties (CONNAUGHTON *et al.*, 1986; PITZER *et al.*, 1984) are significantly better for wider temperature ranges, but may be less useful over the limited range of present interest; these latter expressions are used later. The resultant expressions for these solutes are summarized below:

$$\bar{V}_2^\circ(\text{NaCl, aq}) = 62.333 - 0.09108T - \frac{2012.8}{T-190}\ ;\ \text{0 to 55°C} \qquad (8.24)$$

$$\bar{C}_{p,2}^\circ(\text{NaCl, aq}) = 1885.0 - 4.305T - \frac{73838}{T-190}\ ;\ \text{1 to 45°C} \qquad (8.25)$$

$$\bar{V}_2^\circ(\text{HCl, aq}) = 73.549 - 0.12799T - \frac{1897.9}{T-190}\ ;\ \text{10 to 75°C} \qquad (8.26)$$

$$\bar{C}_{p,2}^\circ(\text{HCl, aq}) = 582.2 - 1.467T - \frac{29356}{T-190}\ ;\ \text{10 to 140°C} \qquad (8.27)$$

Combining the above equations with the present expressions for $NaB(OH)_4$ leads to

$$\bar{V}_2^\circ[\text{B(OH)}_4^-, \text{aq}] = -317.10 + 2.1087T + \frac{114.9}{T-190} - 0.0032292T^2 \qquad (8.28)$$

and

$$\bar{C}_{p,2}^\circ[\text{B(OH)}_4^-, \text{aq}] = 995.5 - 1.4319T - \frac{62978}{T-190} \qquad (8.29)$$

Equilibrium calculations involving these ions over the "low temperature" range should employ these functions rather than the higher temperature extrapolations that are given later.

8.4 Discussion

8.4.1 Literature comparisons

Several authors report the densities of aqueous solutions of boric acid that lead to calculation of the standard state partial molar volumes over a wide range of

temperatures. The most notable of these are the studies by VON ENDRÉDY (1935), [ELLIS (1966) and ELLIS and MCFADDEN (1972)], WARD and MILLERO (1974), CORTI *et al.* (1980), and GRANT-TAYLOR and READ (1988). DEVINA *et al.* (1982) cite many of the Russian high temperature experiments that lead to the standard state partial molar volumes of boric acid from about 25 to 300°C. Results from these cited studies show much larger scatter than any of the presently reported studies and thus will not be included in further discussions. The present results are consistent with the results of ELLIS (1966), VON ENDRÉDY (1935) (wider scatter than other studies), the 45° value from CORTI *et al.* (1980), and in reasonable agreement with the 50°C value from WARD and MILLERO (1974). The results from GRANT-TAYLOR and READ (1988) lead to $\bar{V}^\circ = 45$ cm^3mol^{-1} from 175 to 325°C that decreases to -100 cm^3mol^{-1} at 365°C. These latter results indicate stronger solute-solvent interactions than for other neutral solutes (WHEELER, 1972). Since present applications of these results are not planned above above 300°C, these results were not included in further analysis.

Standard state partial molar volumes of aqueous boric acid, taken from the present work and sources cited in the preceding paragraph, are displayed in Figure 8.5. Assessments (experimental methods, concentration dependence of results, etc.) of all of these results leads us to believe that the present results or those from WARD and MILLERO (1974) are almost certainly the best. Unfortunately, the differences between the present results and those from WARD and MILLERO (1974) are larger than the sum of reasonable estimates of uncertainties for both sets of results. Because the research reported here was done carefully, using methodology that has yielded excellent results for several other systems, we are reluctant to admit that our results are not best. On the other hand, WARD and MILLERO (1974) have used a well-established precise method that also has yielded excellent results for other systems. Further, Millero has a long and admirable record for doing good quality research in this field. As a results of all of these considerations, the selection of recommended "best" standard state partial molar volumes for aqueous boric acid will be postponed until there are new experimental results.[1]

[1]Experiments are underway, J.K. Hovey and L.G. Hepler.

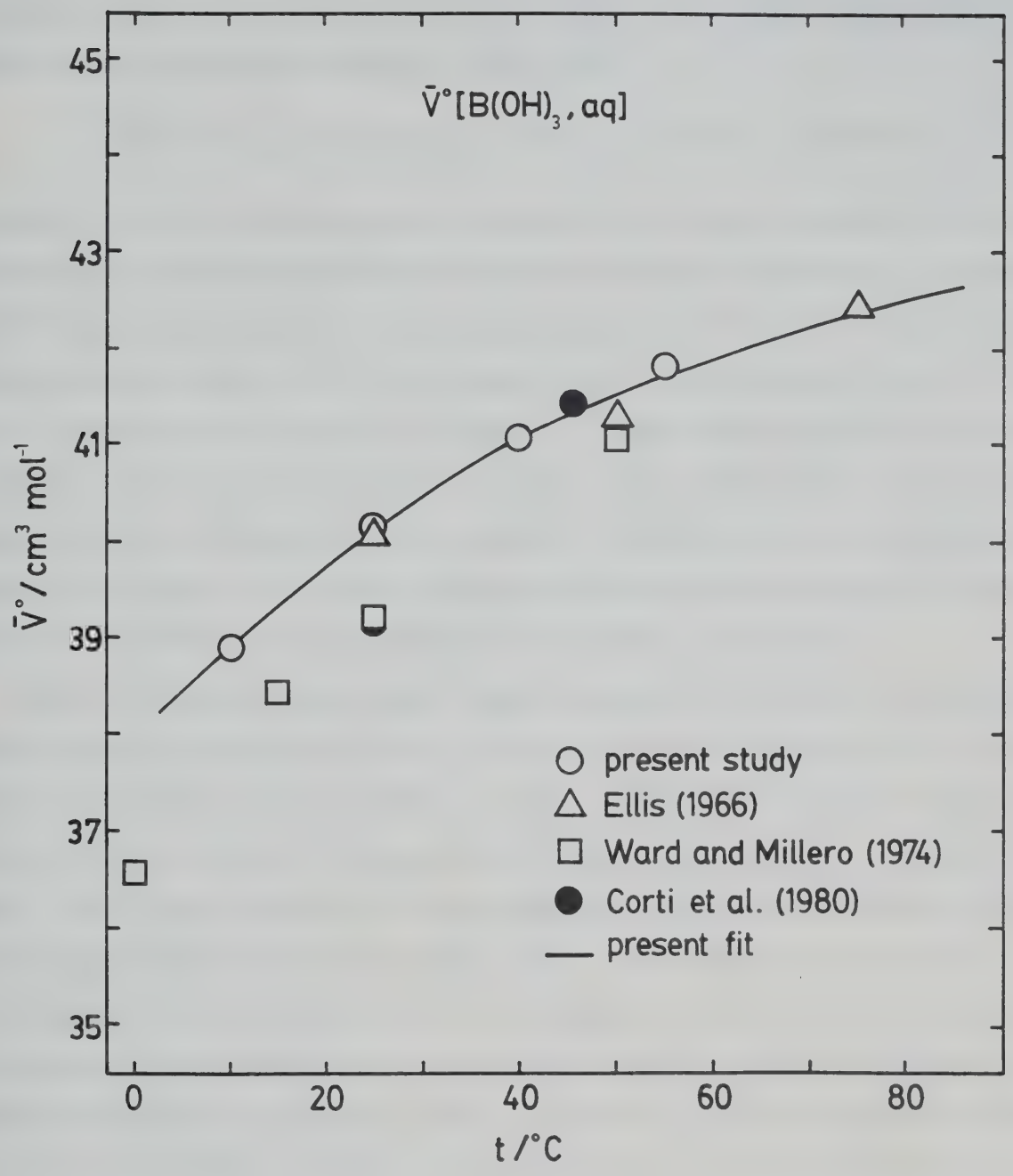


Figure 8.5: Standard state partial molar volumes of aqueous $B(OH)_3$.

Direct measurements of the specific heats of aqueous solutions containing boric acid are cited by DEVINA *et al.* (1982), along with their calculations based on heats of solution of boric acid in water from 15 to 60°C. All of these results were combined to generate the expression (DEVINA *et al.*, 1982):

$$\bar{C}_p^{\circ}[\mathrm{B(OH)_3}]/(\mathrm{J\ K^{-1}mol^{-1}}) = -389.8 + 2.5225T - 0.0028567T^2$$

intended valid over the temperature range of the two sets of results (10 to 260°C). This fitted curve is shown along with the present results in Figure 8.6. As can be seen in the Figure, the results are in poor agreement below 25°C, but are in reasonably good agreement above 25°C. The present value differs from the value of DEVINA *et al.* (1982) at 25° by only 1 $\mathrm{J\ K^{-1}mol^{-1}}$. This suggests that the data from 25 to 60 °C are of very high quality since they were differentiated (with respect to temperature) to obtained the heat capacities. Because of the inaccessibility of data quoted by DEVINA *et al.* (1982) applicable for temperatures above 80°C, fits to only the present results that are considered most reliable, are reported.

There are standard state partial molar volumes for sodium borate from WARD and MILLERO (1974) from 0 to 50°C, CORTI *et al.* (1980) at 25 and 40°C, and results quoted by DEVINA *et al.* (1982) from 25 to 300°C with very large uncertainties. These results are plotted in Figure 8.7 for the present temperature range. DEVINA *et al.* (1982) have derived a fit of the data from WARD and MILLERO (1974) and the Russian high temperature results, that is also shown in Figure 8.7. As can be seen there are substantial differences between all sets of data for this species. It appears that no other direct measurements were done under conditions to ensure that no hydrolyzed species were present. It also appears that further experiments are required to unambiguously define the best volumes at low temperatures. A purely arbitrary decision to use the results from the present study for further discussion and analysis is sufficient here.

Standard state partial molar heat capacities for sodium borate can be derived from various studies of equilibrium constants determined over a wide range of temperatures such as those by MESMER *et al.* (1972), or by enthalpy of solution measurements of boric acid into aqueous solutions containing sodium hydroxide by DEVINA *et al.* (1982). Both approaches require differentiation of the experimental data,

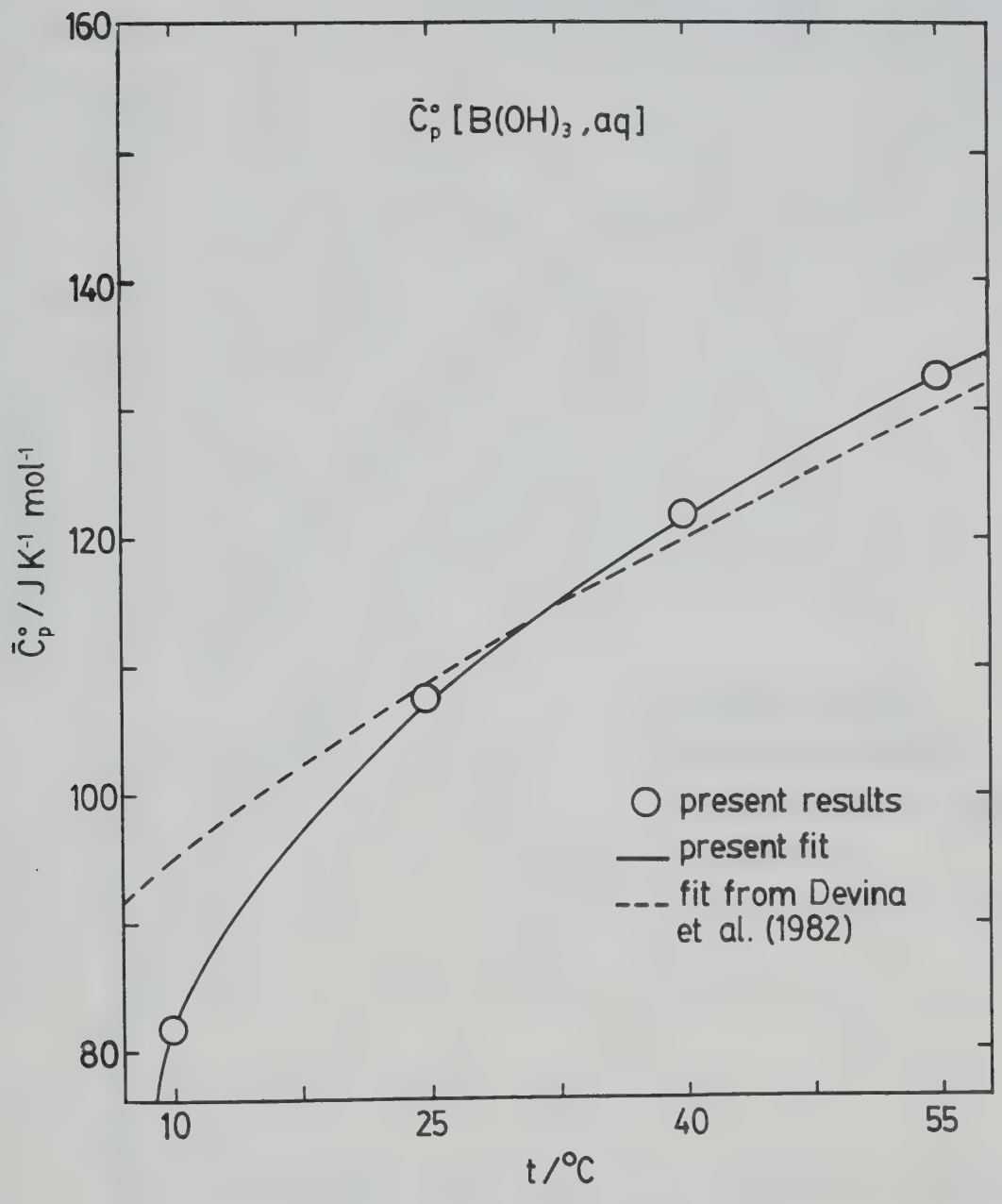


Figure 8.6: Standard state partial molar heat capacities of aqueous $B(OH)_3$.

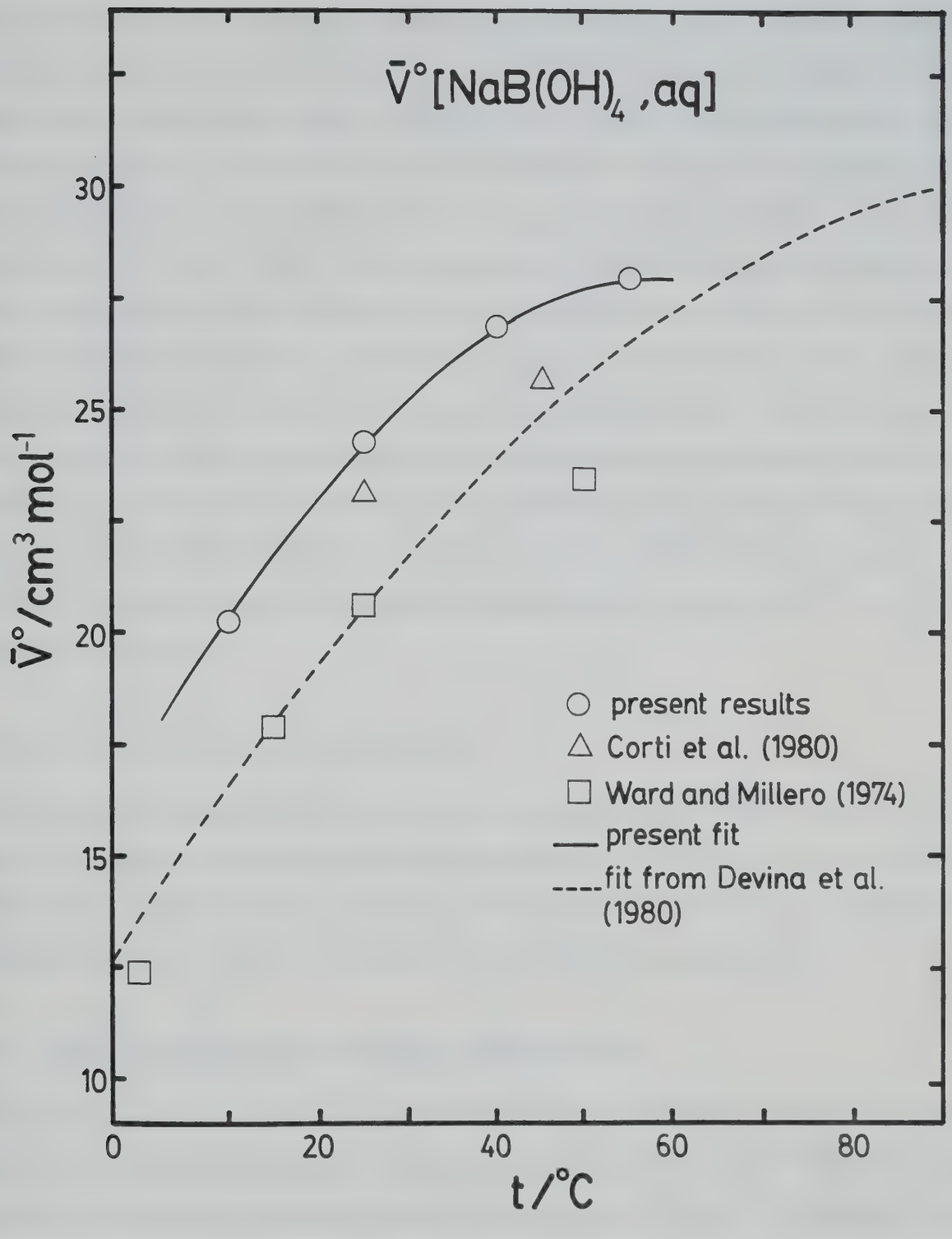


Figure 8.7: Standard state partial molar volumes for aqueous $NaB(OH)_4$.

which normally leads to magnification of uncertainties. Such uncertainties may in some cases be less than those from direct measurements when various problems such as speciation and chemical relaxation are present. Heat capacities measured at high temperatures by SIDOROVA *et al.* (1975) are said to be plagued with the presence of polynuclear borates (DEVINA *et al.*, 1982), and subsequently are not considered further. The present results are plotted in Figure 8.8 along with the results from DEVINA *et al.* (1982) [derived using results from MESMER *et al.* (1972)] and KRYUKOV *et al.* (1973). Good agreement is observed again for temperatures equal to and above 25°C, with the 25°C values differing by only 0.2 J $K^{-1}mol^{-1}$, which is much less than the uncertainty in any one of the values. The differences increase dramatically below 25°C; for example, the difference at 10°C is more than 25 J $K^{-1}mol^{-1}$, which is much larger than the estimated uncertainty in the present values of $\pm$ 3 J $K^{-1}mol^{-1}$. These results clearly show that the equilibrium results, especially those of MESMER *et al.* (1972) are of extraordinarily high accuracy.

Only the present results were used in obtaining the equation for $\bar{C}_p^\circ = f(T)$ that is given by eq. 8.23.

8.4.2 Conventional ionic properties

Standard partial molar properties on the conventional scale [$\bar{V}^\circ(H^+, aq) \equiv 0$; $\bar{C}_p^\circ(H^+, aq) \equiv 0$] have been calculated according to the choices discussed above (the present results in all cases) and are presented in Table 8.6. Standard state partial molar properties for boric acid have been presented in Tables 8.3 and 8.4.

8.4.3 Extrapolations to elevated temperatures

Uses of the equations developed by HELGESON and KIRKHAM (1976) and HELGESON *et al.* (1981) have been described extensively Chapters 4 and 7. These equations describe the temperature (and pressure) dependence of $\bar{C}_p^\circ$ and $\bar{V}^\circ$ in terms of a semi-empirical model based on the Born equation for ion-water interaction. The model has been demonstrated (Chapter 4) to be particularly suited for extrapolation of low temperature data to higher temperatures.

The appropriate equations ignoring the pressure dependence of volumes and heat

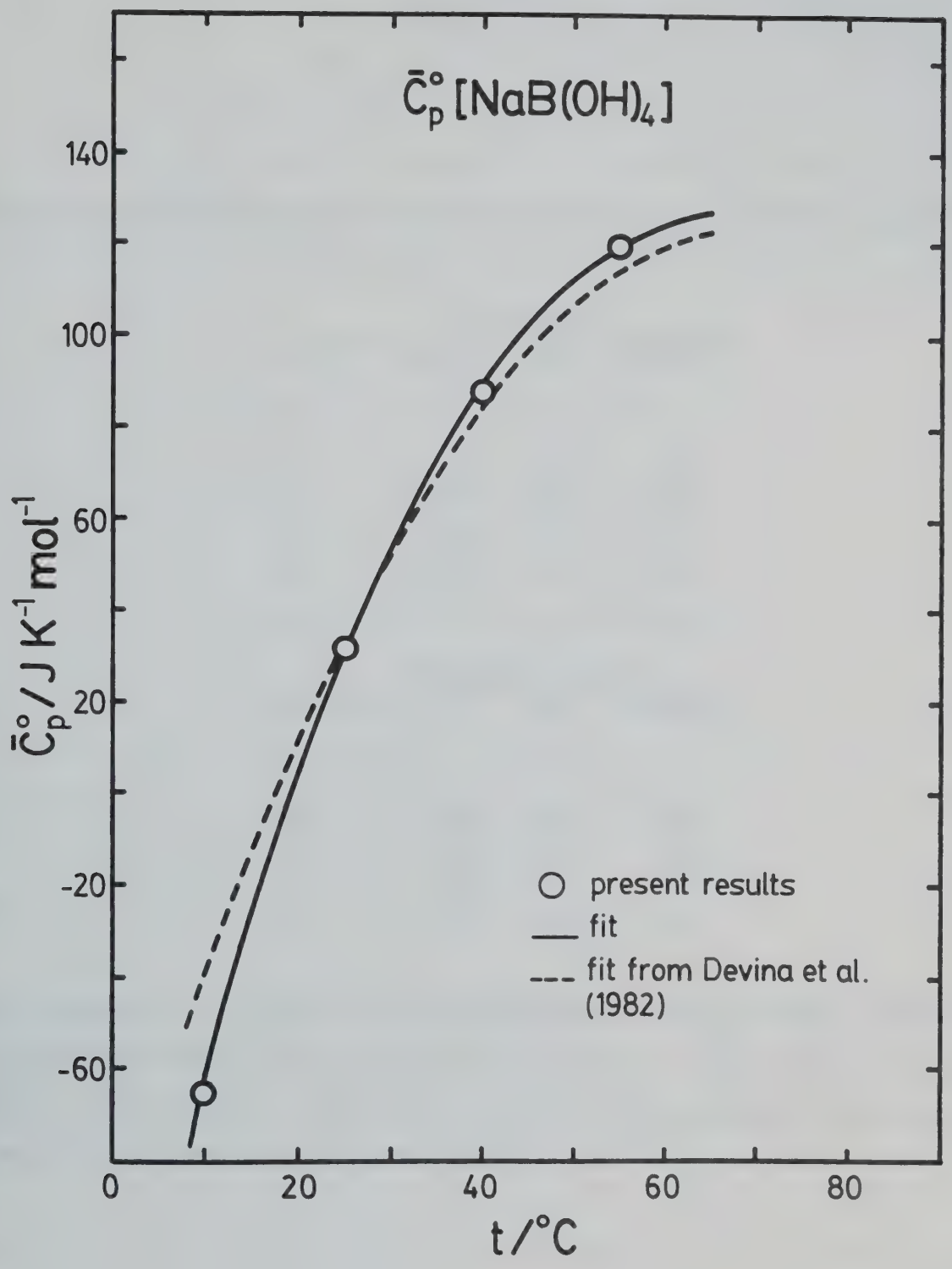


Figure 8.8: Standard state partial molar heat capacities for aqueous $NaB(OH)_4$.

Table 8.5: Standard (conventional) partial molar volumes and heat capacities*

	$\bar{V}°/(\mathrm{cm^3 mol^{-1}})$			
$t/°\mathrm{C}$	H^+	Cl^-	Na^+	$B(OH)_4^-$
10	0	17.15	−2.21	22.53
25	0	17.89	−1.27	25.59
40	0	17.91	−0.44	27.38
55	0	17.81	0.12	27.90

	$\bar{C}_p°/(\mathrm{J\ K^{-1} mol^{-1}})$			
$t/°\mathrm{C}$	H^+	Cl^-	Na^+	$B(OH)_4^-$
10	0	−148.4	21.8	−86.3
25	0	−126.6	42.2	−10.4
40	0	−115.5	52.8	35.1
55	0	−111.7	49.5	70.0

* The values for $Cl^-(aq)$ and $Na^+(aq)$ reported here were taken from TREMAINE *et al.* (1986), MILLERO (1970), ALLRED and WOOLLEY (1981), and PERRON *et al.* (1975) or from expressions reported in Chapter 7 (eqs. 7.25-7.27). The values for $B(OH)_4^-(aq)$ are from this work. The accuracies of these reported values are ± 0.3 $\mathrm{cm^3 mol^{-1}}$ for $\bar{V}°$ and ± 3 $\mathrm{J\ K^{-1} mol^{-1}}$ for $\bar{C}_p°$.

capacities are given below

$$\bar{V}^{\circ}_{T} = \sigma + \frac{\xi T}{T - \theta} + \Delta V_{BORN} \tag{8.30}$$

and

$$\bar{C}^{\circ}_{p,T} = c_1 + \frac{c_2 T}{T - \theta} + \Delta C_{p,BORN} \tag{8.31}$$

where σ, ξ, c_1, c_2, and θ are adjustable parameters. The term $T - \theta$ accounts for the non-Born temperature dependence below 80°C as discussed in Chapter 6. The Born term describes the long range solvent polarization, and becomes the dominant term at high temperatures. The appropriate equations for these Born terms are listed below:

$$\Delta V_{BORN} = -\omega Q \tag{8.32}$$

$$\Delta C_{p,BORN} = \omega T X \tag{8.33}$$

where

$$Q = \left(\frac{\partial \ln \epsilon}{\partial p}\right)_{T} \tag{8.34}$$

$$X = \frac{1}{\epsilon}\left[\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_{p} - \left(\frac{\partial \ln \epsilon}{\partial T}\right)^2_{p}\right] \tag{8.35}$$

$$\omega/(\text{J mol}^{-1}) = 6.9466 \times 10^5 \frac{z^2}{r/\text{Å}} \tag{8.36}$$

Here ϵ is the static dielectric constant of water, z is the charge of the ion and r is the "effective" radius. For monatomic anions the effective radius is the Pauling crystallographic radius and for cations it is the crystallographic radius plus 0.94 Å. Values of X and Q were taken from the tabulations of HELGESON and KIRKHAM (1974, 1976).

As can be seen from the equations described above, the HKF equations results in temperature independent standard state properties for neutral species. As was mentioned earlier in connection with the partial molar volumes of boric acid, the volumes do remain constant from about 175 to 325°C but decrease sharply above 360°C. The following calculations for boric acid are intended for temperatures below which these effects begin. Models that incorporate fractional charges could be used to account for these effects (SHOCK, 1987) but it was not deemed appropriate here because of the desire to limit the applicability of the expressions to less than 300°C. Observations about the divergence of these properties is deferred until after properties for one other neutral solute (UO_2SO_4) are obtained.

The effective radius used for $B(OH)_4^-(aq)$ was calculated from the effective ionic radii given by SHANNON (1976) by adding the radius of B^{3+} to the radius of two water molecules or OH^- ions. This calculation resulted in the value $r = 2.81$ Å. Least squares fits to the standard state volumes and heat capacities in Tables 8.3 and 8.4 yield the following expressions

$$\frac{\bar{V}^\circ_{2,T}[NaB(OH)_4,\ aq]}{(cm^3mol^{-1})} = 43.447 - \frac{2.8911\ T}{T-242} - 6.0528 \times 10^6 Q \qquad (8.37)$$

$$\frac{\bar{C}_{p,2,T}[NaB(OH)_4,\ aq]}{(J\ K^{-1}mol^{-1})} = 431.24 - \frac{64.4239\ T}{T-242} + 6.0528 \times 10^5 TX \qquad (8.38)$$

$$\frac{\bar{V}^\circ_{2,T}[B(OH)_3,\ aq]}{(cm^3mol^{-1})} = 50.090 - \frac{3.2124\ T}{T-202} \qquad (8.39)$$

$$\frac{\bar{C}_{p,2,T}[B(OH)_3,\ aq]}{(J\ K^{-1}mol^{-1})} = 200.41 - \frac{18.4914\ T}{T-239} \qquad (8.40)$$

Here Q and X are in units of bar^{-1} and K^{-2}, respectively. All equations were generated from least squares fits to the present data except for the fit to the standard state volumes of boric acid where the present data were combined with the high temperature results of ELLIS (1966). The θ values are usually taken to be equal for all standard state properties as required by the HKF model. However, it was necessary here to fit to separate θ values for the volumes and heat capacities. This fitting procedure is not new and is described in Chapter 7 and the following section.

The high temperature equilibrium calculations that follow in the next section require similar extrapolations for HCl(aq). These functions have been reported by HELGESON *et al.* (1981), but as shown in Chapter 7, more recent data can be used for such calculations.

For HCl(aq), volumetric data from HERRINGTON *et al.* (1985) and ALLRED and WOOLLEY (1981), were used [but not the data from AKERLOF and TEARE (1938) or ELLIS and MCFADDEN (1968)] to generate the extrapolation equations. The heat capacity parameters for HCl(aq) were taken from TREMAINE *et. al.* (1986) whose data are consistent with the measurements of SALUJA *et al.* (1986). It was not possible to use the same value of θ to fit both the volume and heat capacity functions for HCl(aq); therefore independent values θ_V and θ_J were assigned. The

results of the fits to these data are summarized below.

$$\frac{\bar{V}^{\circ}_{2,T}(\mathrm{HCl,\ aq})}{(\mathrm{cm^3 mol^{-1}})} = 23.39 - \frac{0.2446\ T}{T - 259} - 6.093 \times 10^6 Q \qquad (8.41)$$

$$\frac{\bar{C}_{p,2,T}(\mathrm{HCl,\ aq})}{(\mathrm{J\ K^{-1} mol^{-1}})} = 14.22 - \frac{14.52\ T}{T - 246} + 6.093 \times 10^5 TX \qquad (8.42)$$

8.4.4 Equilibrium calculations

The most obvious calculation to be done with the present data is the calculation of high temperature equilibrium constants for ionization of boric acid, using the present equations that are based on relatively low temperature data. There are numerous studies that report both the temperature MANOV *et al.*, 1944; OWEN and KING, 1943; MESMER *et al.*, 1972; KRYUKOV *et al.*, 1973) and pressure (DISTÈCHE and DISTÈCHE, 1967; CULBERSON and PYTKOWICZ, 1968) dependence of the equilibrium constant for this ionization reaction.

The equilibrium constant for a reaction at high temperatures and pressures can be calculated from the Gibbs free energy change. The Gibbs free energy at high temperatures and pressures is related to that for some reference temperature and pressure (298.15K, 1bar) by

$$\Delta G^{\circ}_T = \Delta G^{\circ}_{f,298} - \bar{S}^{\circ}_{298}(T - 298.15) + \int_{298}^{T} \bar{C}^{\circ}_p dT - T \int_{298}^{T} \frac{\bar{C}^{\circ}_p}{T} dT + \int_1^p \bar{V}^{\circ} dp \qquad (8.43)$$

The ionization of boric acid in water can be represented by the following reaction equation

$$\mathrm{B(OH)_4^-(aq) + H^+(aq) = B(OH)_3(aq) + H_2O(l)} \qquad (8.44)$$

Values of the Gibbs free energies of formation, and the standard state entropies at 298.15 K and 1 bar are given in Table 8.6 for all of the species required in calculations for the equilibrium represented by eq. 8.44. The change in the standard state properties for the reaction represented by eq. 8.44 can be calculated by the equation

$$\Delta Y^{\circ} = \bar{Y}^{\circ}[\mathrm{B(OH)_3}] + \bar{Y}^{\circ}[\mathrm{H_2O}] + \bar{Y}^{\circ}[\mathrm{NaCl}] - \bar{Y}^{\circ}[\mathrm{NaB(OH)_4}] - \bar{Y}^{\circ}[\mathrm{HCl}] \qquad (8.45)$$

High temperature Gibbs free energies were calculated from expressions of the type given by eq. 8.43 for $\mathrm{NaB(OH)_4(aq)}$ and $\mathrm{B(OH)_3(aq)}$ from the present work, HCl(aq)

Table 8.6: Standard state Gibbs free energies of formation and entropies at 25°C from WAGMAN *et al.* (1982)

Species	ΔG_f° kJ mol^{-1}	$\bar{S}^\circ$ J K^{-1}mol^{-1}
$B(OH)_4^-(aq)$	−1153.17	102.5
$B(OH)_3(aq)$	−968.75	162.3
$Na^+(aq)$	−261.905	59.0
$Cl^-(aq)$	−131.228	56.5
$H_2O(l)$	−237.129	69.91
$H^+(aq)$	0	0

from TREMAINE *et al.* (1986), values for NaCl(aq) were taken directly from PITZER *et al.* (1984) and the values for water were taken from HELGESON and KIRKHAM (1974). The calculated values of the equilibrium constants for this reaction to 300°C are shown in Figure 8.9. The values of the equilibrium constants from MESMER *et al.* (1972) were combined with values for the dissociation of water (SWEETON *et al.*, 1974) to generate these values that are also plotted in Figure 8.9.

As can be seen in Figure 8.9, the results calculated from the present heat capacity and volume functions obtained from 10 to 55°C are in excellent agreement with all of the "best" results to 100°C and reasonable agreement to 300°C. The equilibrium constants derived using room temperature enthalpy and entropy changes for this reaction as listed in Table 8.6, differed by at most 0.04 in $\log K$ from the results of MESMER *et al.* (1972) over the entire temperature range to 300°C. Most of this discrepancy at temperatures below 250° comes from differences in $\Delta S°$ for the reaction given by eq. 8.44 derived from values in Table 8.6 and the $\Delta S°$ value determined by MESMER *et al.* (1972). Calculations using the $\Delta S°$ value determined by MESMER *et al.* (1972) at 298.15 K are in even better agreement over the temperature range to about 290°C and are shown in Figure 8.9. These latter calculations deviate from the results of MESMER *et al.* (1972) by no more than 0.01 in log K - which is equal to the expected uncertainties in the fitting equation used by MESMER *et al.* (1972). It is again apparent that heat capacities and volumes measured over a relatively narrow temperature range (10 to 55°C) can be used to provide data that agree with the "best" high temperature studies. The comparisons here and in Chapter 4, lend confidence to this approach and suggest that the technique may be used in calculations for which high temperature experimental results are either unattainable or unknown. Examples of this approach are provided in Chapter 10.

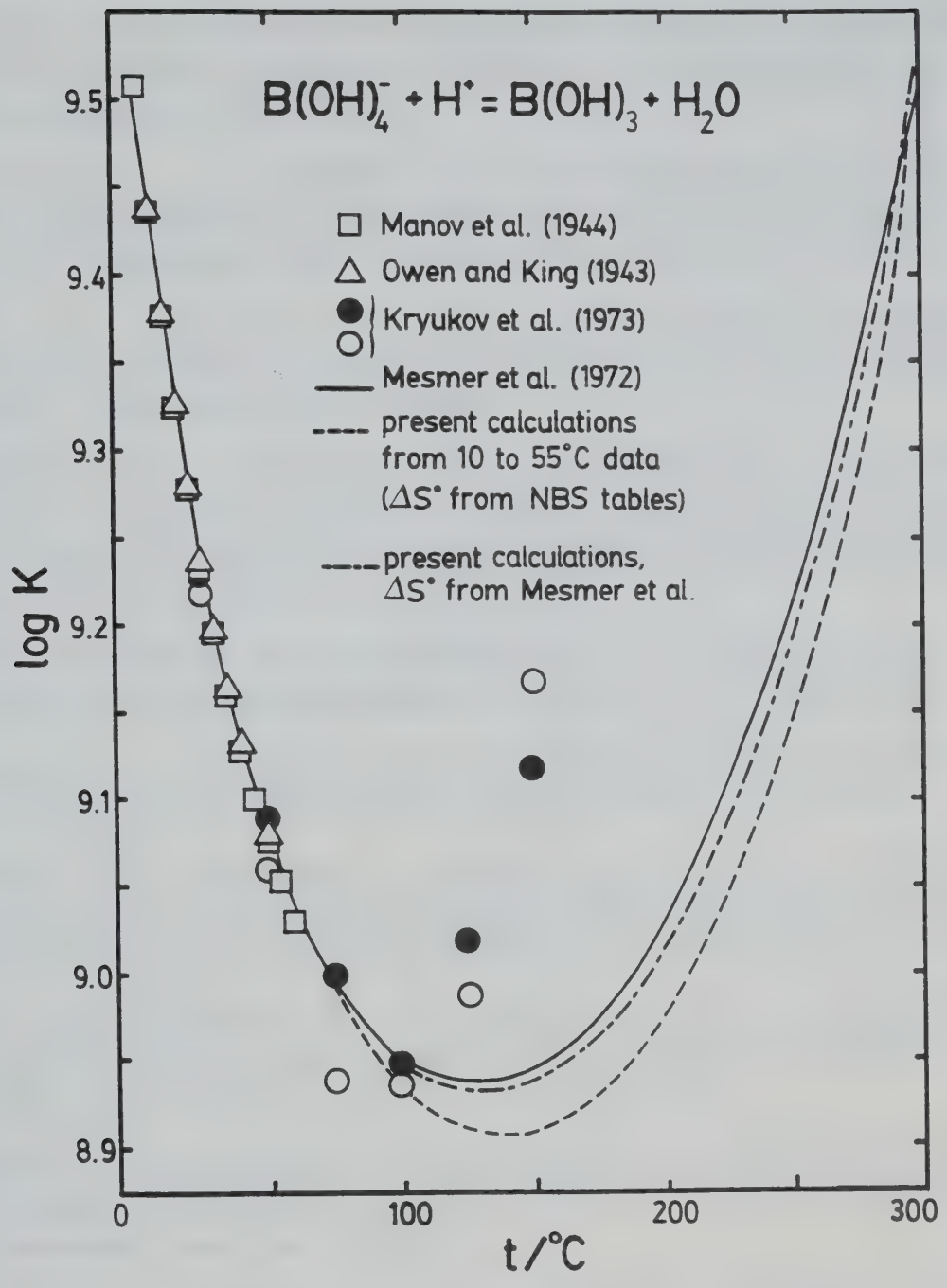


Figure 8.9: Comparison of equilibrium constants for the ionization of boric acid. Predictions using the present data obtained to 55°C are compared with direct results to 300°C.

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Chapter 9

Thermodynamics of aqueous iron(II) and iron(III): Heat capacities and volumes of aqueous ferrous perchlorate and ferric perchlorate from 10 to 55°C. Prediction of the standard electrode potential for the ferric-ferrous ion couple to 300°C.

9.1 Introduction

Hundreds of authors have reported thermodynamic properties applicable to iron(II) and iron(III) aqueous systems. The iron-water system, however, is plagued with inconsistencies in many of the currently available thermodynamic data. Several comprehensive reviews of thermodynamic data pertaining to species in the iron-water system are available (BAES and MESMER, 1976; LANGMUIR, 1969; SYLVA, 1972), yet the thermodynamic properties for many species of both iron(II) and iron(III), particularly hydrolyzed species, are not well known.

Conprehensive solubility studies involving magnetite (Fe_3O_4) have been reported by SWEETON and BAES (1970) and TREMAINE and LEBLANC (1980). Estimates of thermodynamic properties for some iron(II) and iron(III) hydrolyzed species have resulted from these works. There are, however, some discrepancies in results of these studies, presumably due to the difficulty in determining solubilities of very sparingly soluble metal oxides and also because of the presence of both iron(II) and iron(III) in many of these experiments.

HEPLER and co-workers (LARSON *et al.*, 1968; CERUTTI and HEPLER, 1977) have shown by using solubility and calorimetric data that the standard potentials of the iron-iron(III), and iron-iron(II) couples are significantly different when calculated by way of these "thermal" data than when measured electrochemically. It is apparent now that the approach of HEPLER *et al.* is best for determining these standard

potentials. Probable errors in electrochemical determinations of these potentials have been attributed to "irreversible" electrodes. The standard state entropies of Fe^{2+}(aq) and Fe^{3+}(aq) are quite well known from these results (the former *much* more so than the latter). CERUTTI and HEPLER (1977) have further demonstrated discrepancies in existing thermodynamic data for Fe^{2+}(aq) by careful measurements of the heats of solution of $FeCl_2$(c).

The present work provides results leading to standard state partial molar heat capacities and volumes of Fe^{2+}(aq) and Fe^{3+}(aq) from to 10 to 55°C. A large fraction of the interest in these results comes from classical thermodynamic calculations that can be done with the results. In this context, calculations of the high temperature equilibrium properties of aqueous iron(II) and iron(III), and the refinement of room temperature free energies, enthalpies, and entropies are of interest. These data are also useful in the development and testing of theoretical and semi-theoretical models for the prediction of the standard state heat capacities and volumes of aqueous species as discussed previously in Chapter 3.

9.2 Experimental

Water used for all experiments was first passed through an activated charcoal filter and then through a Milli-RO4/Milli-Q reagent grade mixed bed ion exchange and activated carbon system to yield purified water with a resistivity of 18 MΩ cm or greater.

Solutions of NaCl (Fisher certified, ACS) were prepared by mass after drying the salt at 120 °C until constant weight. Ferrous perchlorate hexahydrate was obtained from ÆSAR (Johnson Matthey) certified 99+% and was used without further purification. Two different samples of ferric perchlorate hexahydrate were used. One was obtained from Strem (99.5+%) and the other from Alfa (≈ 95%). Both of these samples were recrystallized once from dilute perchloric acid (sufficient to avoid hydrolysis).

The stock solution of ferrous perchlorate was prepared by first dissolving the crystals in very dilute perchloric acid, followed by filtration to remove very small amounts of particulate matter, and finally dilution with (standardized) perchloric

acid (by mass) to the desired stock solution concentration. All handling of ferrous perchlorate was done quickly, and under a helium atmosphere. This stock solution was analyzed by titration with a standard solution of potassium dichromate (VOGEL, 1978) and subsequent analyses were performed daily until completion of the calorimetric runs. The original crystals of ferrous perchlorate were analyzed for total iron by the method of SCHWARZENBACH (1957) that involved oxidation of all iron to the 3+ state with persulphate and subsequent titration of the iron with a solution of EDTA at 40°C in the presence of salicylic acid and glycine. The EDTA solution had been standardized with a weighed amount of pure Zn metal dissolved in HCl. It was found that 0.3% of the total iron in the original solid sample was in the 3+ state. The amounts of iron(III) in the solutions of ferrous perchlorate were determined by daily titrations of combinations of stock or diluted solutions with potassium dichromate [to monitor Fe(II) directly], and with EDTA (to monitor total iron). It was found that the ferrous perchlorate solutions contained amounts of ferric ion representing 0.5 to 1.1% of the total iron over the course of the measurements. The experimental results were corrected for these small amounts of iron(III) as discussed in following sections. The amount of excess perchloric acid in the stock solution was calculated from careful pH measurements referenced to the standardized perchloric acid solution used for dilution of the stock solution (pH $\approx$ 4) converted to the same total ionic strength as the stock solution with sodium perchlorate. Amounts of excess perchloric acid in the solutions were calculated daily from the results of analytical determinations for iron(II) and total iron. These amounts changed because of the increasing amounts of iron(III) as time progressed through the course of the measurements. More dilute solutions were all prepared by mass by dilution with standardized 10^{-4} m $HClO_4$.

Two ferric perchlorate stock solutions were prepared by dissolving the two samples of recrystallized ferric perchlorate hexahydrate into dilute ($\approx$ 0.3-0.4 m) solutions of perchloric acid. The amount of iron(III) in the stock solutions was determined by titrations with EDTA to a thiocyanate endpoint (SHWARZENBACH and FLASCKA, 1969). Total perchlorate in the stock solution ($3m_2 + m_3$), where m_2 and m_3 are the molalities of ferric ion and perchloric acid, respectively, was determined by passing weighed aliquots of the solution through an ion exchange resin [Rexyn 101(H)] and titrating the eluent with a standard solution of sodium hydrox-

ide. Excess perchlorate or total perchloric acid in the stock solution was obtained by difference. Subsequent solutions were prepared by mass by dilution of the stock solutions with a standard solution of 0.4 m $HClO_4$. Tests of both stock solutions of iron(III) with o-phenanthroline showed no detectable amounts of iron(II).

The densities of all solutions were measured relative to water at each of the experimental temperatures ± 0.01 °C with a Sodev 03D vibrating tube densimeter (PICKER *et al.*, 1974), which was calibrated with pure water and a standard solution of NaCl. Densities of the standard NaCl solutions were determined from the data listed by MILLERO (1970). Heat capacities were measured relative to water with a Sodev CP-C Picker type flow microcalorimeter (PICKER *et al.*, 1971). Temperatures were maintained (constant to ± 0.001°C) with separate Sodev CT-L circulating baths and monitored with calibrated thermistors. Daily evaluation of the calorimetric heat loss correction factor (DESNOYERS *et al.*, 1976) by way of measurements on standard solutions of NaCl led to $f = 1.007 \pm 0.001$ at 25°C. This heat loss factor was assumed to be independent of temperature (TREMAINE *et al.*, 1986).

9.3 Results

9.3.1 Apparent molar properties

Aqueous solutions of ferrous perchlorate contain iron in the form of $Fe^{2+}(aq)$ in sufficiently acidic solutions. In less acidic solutions the iron is present as $FeOH^{+}(aq)$ and in still less acidic or alkaline solutions the iron precipitates as the solid hydroxide. Of specific interest here is the first hydrolysis reaction represented by

$$Fe^{2+}(aq) + H_2O(l) = FeOH^{+}(aq) + H^{+}(aq) \qquad (9.1)$$

Calculations based on equilibrium constants from BAES and MESMER (1976) have indicated that $\approx 10^{-4}$ molal acid is sufficient to ignore the formation of $FeOH^{+}(aq)$ that maximizes the iron present in its presently desired state, $Fe^{2+}(aq)$. Because the added acid complicates resulting data treatments, it is most advantageous to use as small amounts as possible.

In strongly acidic solutions, iron in aqueous solutions of ferric perchlorate is predominantly in the form $Fe^{3+}(aq)$. In slightly less acidic solutions some of the iron

is in the form $FeOH^{2+}(aq)$ and in still less acidic solutions there are further complications. Because the primary interest is in the properties of $Fe^{3+}(aq)$, moderately acidic solutions have to be used in order to keep some large fraction of the Fe(III) in the form of $Fe^{3+}(aq)$. Consideration of the equilibrium

$$Fe^{3+}(aq) + H_2O(l) = FeOH^{2+}(aq) + H^+(aq) \tag{9.2}$$

and associated equilibrium constants from BAES and MESMER (1976) have led to the deduction that concentrations of perchloric acid larger than ≈ 0.3 molal are required to keep the ratio $(Fe^{3+}/FeOH^{2+})$ greater than 0.99. These large concentrations of "auxiliary" electrolyte (in this case acid) were kept at the minimum allowable level to reduce difficulties associated this added electrolyte whilst maintaining most of the iron in the presently desired state, $Fe^{3+}(aq)$.

Values of the density and specific heat capacity of pure water at each of the experimental temperatures (KELL, 1967; 1972) are listed in Chapter 4, Table 4.2. The experimentally determined relative densities $(d - d_1^\circ)$ and heat capacity ratios $(c_p d/c_{p,1}^\circ d_1^\circ$ - 1) for all of the aqueous solutions containing $Fe(ClO_4)_3$ and $HClO_4$ are listed in Table 9.2 and results for solutions containing $Fe(ClO_4)_2$ and $HClO_4$ are listed in Table 9.3. The "experimental" apparent molar property ${}^\phi Y^{exptl}$ of all of these solutions that contain more than one solute is defined generally by

$${}^\phi Y^{exptl} = \frac{Y_{soln} - 55.509 Y_1^\circ}{\sum m_i} \tag{9.3}$$

where Y_{soln} is the extensive property (volume or heat capacity) of a solution that contains one kilogram of solvent (water), Y_1° is the molar volume or heat capacity of pure solvent (water), and m_i is the molality of species i. Experimental apparent molar volumes and heat capacities were calculated from the direct results of experiments by

$${}^\phi V^{exptl} = \frac{\dfrac{1 + \sum m_i M_i}{d} - \dfrac{1}{d_1^\circ}}{\sum m_i} \tag{9.4}$$

and

$${}^\phi C_p^{exptl} = \frac{c_p(1 + \sum m_i M_i) - c_{p,1}^\circ}{\sum m_i} \tag{9.5}$$

In these equations M_i represents the molar mass of solute i, c_p and d are the specific heat capacity and density of the solution, and $c_{p,1}^\circ$ and d_1° are the specific heat capacity

and density of pure water. Direct experimental results and calculated experimental apparent molar volumes and heat capacities are listed in Tables 9.1 and 9.2.

There are complications associated with deriving the desired apparent and partial molar properties from the defined experimental properties. First the presence of non-negligible molalities of perchloric acid in the ferric perchlorate solutions must be considered. For the ferrous perchlorate solutions the presence of perchloric acid and also ferric perchlorate that has resulted from the unintended oxidation of $Fe^{2+}(aq)$ must also be considered. Therefore the data treatment begins by analyzing the $Fe(ClO_4)_3 + HClO_4$ solutions to obtain the desired properties of $Fe(ClO_4)_3$ and then use these values for analysis of the properties of $Fe(ClO_4)_2$ solutions that contain small amounts of $Fe(ClO_4)_3$ and $HClO_4$.

Ferric perchlorate

Young's rule (YOUNG and SMITH, 1954) provides a basis for expressing the experimental apparent molar properties of solutions containing ferric perchlorate and perchloric acid in terms of the properties of the individual components:

$$^{\phi}Y^{exptl} = \frac{m_2}{m_2 + m_3}{}^{\phi}Y_2 + \frac{m_3}{m_2 + m_3}{}^{\phi}Y_3 + \delta_{23}^{Y} \tag{9.6}$$

Here ${}^{\phi}Y_2$ and ${}^{\phi}Y_3$ apply at the total ionic strength of the solution, and δ_{23}^{Y} is an excess mixing term having the form (YOUNG and SMITH, 1954):

$$\delta_{23}^{Y} = k_{23}\frac{m_2 m_3}{(m_2 + m_3)^2} I \tag{9.7}$$

The apparent molar volumes and heat capacities of these solutions are assumed to be well represented by extended Debye-Hückel equations of the type derived in Chapter 4:

$${}^{\phi}Y_2 = \bar{Y}_2^{\circ} + \frac{3}{2}\omega A_Y \left(\frac{1}{\Lambda} - \frac{\sigma}{3}\right) I^{1/2} + B_Y I + C_Y I^{3/2} \tag{9.8}$$

In this equation symbols have the following meanings:

$$I = \omega m = \frac{1}{2}\sum m_i z_i^2 \tag{9.9}$$

$$\Lambda = 1 + I^{1/2} \tag{9.10}$$

$$\sigma = \frac{3\left(\Lambda - \frac{1}{\Lambda} - 2\ln\Lambda\right)}{I^{3/2}} \tag{9.11}$$

Table 9.1: Compositions of solutions and experimental apparent molar volumes and heat capacities for $Fe(ClO_4)_3/HClO_4$ mixtures.

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	ϕV^{exptl} (cm^{3}mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	ϕC_p^{exptl} (J K^{-1}mol^{-1})
		10°C Strem			
0.1987	0.1926	6.1309	68.424	−3.345	−84.03
0.1606	0.2216	5.3437	63.841	−3.045	−77.17
0.1218	0.2511	4.5330	59.092	−2.743	−69.91
0.09333	0.2727	3.9412	55.294	−2.519	−64.83
0.07145	0.2894	3.4817	52.373	−2.337	−59.30
0.05404	0.3026	3.1117	50.087	−2.193	−54.41
0.04250	0.3114	2.8728	48.354	−2.092	−51.33
0.01728	0.3306	2.3404	44.735	−1.878	−44.11
		25°C Strem			
0.1987	0.1926	5.9362	73.051	−2.850	−11.02
0.1606	0.2216	5.1691	68.125	−2.636	−14.12
0.1218	0.2511	4.3854	62.829	−2.397	−15.26
0.09333	0.2727	3.8037	58.872	−2.217	−15.25
0.07145	0.2894	3.3545	55.752	−2.059	−12.79
0.05404	0.3026	2.9970	53.188	−1.934	−11.02
0.04250	0.3114	2.7595	51.455	−1.859	−10.75
0.01728	0.3306	2.2386	46.598	−1.678	−8.16
		25°C Alfa			
0.1417	0.1770	4.5114	68.419	−2.284	−23.28
0.1179	0.2050	4.0749	64.127	−2.179	−22.82
0.09492	0.2321	3.6495	60.156	−2.073	−21.51
0.07222	0.2588	3.2268	56.390	−1.950	−17.80
0.05574	0.2782	2.9202	53.695	−1.860	−15.02
0.04058	0.2960	2.6381	51.235	−1.785	−13.74
0.02573	0.3135	2.3622	48.848	−1.695	−10.36
0.01314	0.3283	2.1263	46.903	−1.626	−8.30

Table 9.1: continued.

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	ϕV^{exptl} (cm^{3}mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	ϕC_p^{exptl} (J K^{-1}mol^{-1})
			40°C Strem		
0.1987	0.1926	5.7914	76.333	−2.6256	25.59
0.1606	0.2216	5.0409	71.133	−2.4617	16.39
0.1218	0.2511	4.2634	65.829	−2.2665	10.77
0.09333	0.2727	3.6976	61.555	−2.107	7.39
0.07145	0.2894	3.2547	58.346	−1.976	6.49
0.05404	0.3026	2.9076	55.558	−1.860	6.48
0.04250	0.3114	2.6702	53.868	−1.789	6.51
0.01728	0.3306	2.1625	49.726	−1.620	6.67
			55°C Strem		
0.1987	0.1926	5.7066	78.036	−2.420	53.27
0.1606	0.2216	4.9634	72.773	−2.312	38.05
0.1218	0.2511	4.1948	67.364	−2.159	27.66
0.09333	0.2727	3.6334	63.067	−2.017	22.48
0.07145	0.2894	3.1973	59.748	−1.904	19.23
0.05404	0.3026	2.8533	56.933	−1.815	15.90
0.04250	0.3114	2.6226	55.093	−1.749	14.89
0.01728	0.3306	2.1166	50.988	−1.590	14.22

Table 9.2: Compositions of solutions and experimental apparent molar volumes and heat capacities for $Fe(ClO_4)_2(m_2)$ / $HClO_4(m_3)$ / $Fe(ClO_4)_3(m_4)$ mixtures.

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	m_4 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	ϕV^{exptl} (cm^{3}mol^{-1})	$-10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	ϕC_p^{exptl} (J K^{-1}mol^{-1})
			10°C			
0.5429	0.04357	0.00392	10.2300	64.146	4.191	−42.49
0.4208	0.03383	0.00304	8.0237	63.559	3.411	−57.76
0.3124	0.02518	0.00225	6.0208	62.994	2.649	−72.43
0.2482	0.02005	0.00179	4.8219	62.320	2.158	−82.32
0.1952	0.01582	0.00141	3.8083	62.226	1.737	−89.35
0.1433	0.01168	0.00103	2.8097	61.959	1.308	−98.06
0.09728	0.08009	0.00070	1.9169	61.670	0.9129	−107.91
0.05184	0.04384	0.00037	1.0297	60.866	0.4993	−119.00
			25°C			
0.5440	0.04467	0.00281	9.9338	68.516	3.721	9.79
0.4217	0.03468	0.00218	7.7849	68.165	2.994	0.344
0.3131	0.02581	0.00162	5.8385	67.784	2.298	−8.39
0.2487	0.02055	0.00129	4.6682	67.459	1.858	−13.50
0.1956	0.01622	0.00101	3.6919	67.184	1.494	−20.09
0.1436	0.01197	0.00074	2.7242	66.958	1.117	−25.27
0.09747	0.008207	0.00050	1.8606	66.513	0.7776	−33.52
0.05195	0.004489	0.00027	0.9975	66.104	0.4276	−43.40

Table 9.2: continued.

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	m_4 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	ϕV^{exptl} (cm^{3}mol^{-1})	$-10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	ϕC_p^{exptl} (J K^{-1}mol^{-1})
			40°C			
0.5418	0.04246	0.00502	9.6817	72.44	3.533	37.14
0.4200	0.03297	0.00389	7.5876	72.148	2.824	30.25
0.3118	0.02454	0.00289	5.6877	71.916	2.157	23.81
0.2477	0.01954	0.00229	4.5461	71.693	1.749	18.68
0.1948	0.01543	0.00180	3.5924	71.587	1.394	15.72
0.1430	0.01139	0.00133	2.6477	71.588	1.042	11.81
0.09708	0.007812	0.00090	1.8058	71.423	0.7306	3.06
0.05173	0.004278	0.00048	0.9650	71.603	0.3983	−1.32
			55°C			
0.5407	0.04136	0.00612	9.5602	74.013	3.470	45.71
0.4191	0.03212	0.00475	7.4864	73.874	2.773	39.64
0.3112	0.02391	0.00352	5.6072	73.798	2.120	33.71
0.2472	0.01904	0.00280	4.4804	73.632	1.699	32.11
0.1944	0.01503	0.00220	3.5407	73.530	1.377	24.53
0.1427	0.01110	0.00162	2.6031	73.970	1.033	21.48
0.09688	0.007614	0.00110	1.7733	71.391	0.7044	8.34
0.05163	0.004173	0.00058	9.3407	76.683	0.3896	23.59

Values for the Debye-Hückel limiting slopes (A_Y) were taken from Ananthaswamy and Atkinson and are listed in Table 9.3.

Apparent molar volumes and heat capacities for $HClO_4$ from 10 to 55°C were taken from Chapter 4. Expressions of the type given by eqs. 9.6-9.11 were fitted to the experimental apparent molar properties listed in Table 9.1 to generate the values of $\bar{Y}_2^\circ$, B_Y and k_{23}^Y for the mixtures of $Fe(ClO_4)_3$ and $HClO_4$.

The temperature dependence of the B_Y and k_{23}^Y parameters were represented by quadratic equations of the form

$$B_Y(\text{ or } k_{23}^Y) = p_1 + p_2T + p_3T^2 \tag{9.12}$$

without significant loss in the precision of the data fits. The p_i terms are fitting coefficients and T is the temperature in kelvins. Then, using constrained values of B_Y and k_{23}^Y that are listed in Table 9.3, equations of type 9.6 were fitted to the experimental data to obtain the infinite dilution standard state properties that are also listed in Table 9.3. Listed uncertainties in Table 9.3 are those that result from unconstrained fits.

Uncertainties in the derived values of ${}^\phi V_2^\circ$ and ${}^\phi C_{p,2}^\circ$ for $Fe(ClO_4)_3$ are larger than most of the uncertainties reported elsewhere in this thesis for these same properties of other electrolytes. These unusually large uncertainties are due mostly to the relatively long extrapolations to zero ionic strength necessary because of the minimum ionic strength of more than 0.3 molal imposed by the minimum molality of perchloric acid required to suppress hydrolysis. Similarly large uncertainties are to be expected whenever large concentrations of acid or base must be used to minimize hydrolysis reactions.

Plots of ${}^\phi Y_2$ minus the Guggenheim form of the Debye-Hückel limiting law (shown in eq. 9.8) are presented in Figures 9.1 and 9.2 for the derived apparent molar properties of $Fe(ClO_4)_3$(aq). The ability of the above described procedure to represent the high concentration behaviour and the standard state values (infinite dilution) is illustrated by these plots.

Table 9.3: Standard state partial molar volumes, heat capacities, and ionic strength parameters for $Fe(ClO_4)_3(aq)$.*

t (°C)	${}^{\phi}V_2^{\circ}$ (cm^3mol^{-1})	A_V ($cm^3kg^{1/2}mol^{-3/2}$)	B_V ($cm^3kg\ mol^{-2}$)	k_{23}^V ($cm^3kg\ mol^{-2}$)
10	88.5 ± 1.2	1.6420	-0.398 ± 0.6	-1.211 ± 2.7
25	98.4 ± 0.8	1.8743	-0.482 ± 0.3	-6.244 ± 1.7
25 Alfa	95.8 ± 0.2	1.8743	-0.482 ± 0.3	-6.244 ± 1.7
40	101.7 ± 1.6	2.1540	-0.978 ± 0.6	-5.336 ± 3.2
55	99.2 ± 1.3	2.4946	-1.883 ± 0.4	1.513 ± 2.5

t (°C)	${}^{\phi}C_{p,2}^{\circ}$ ($JK^{-1}mol^{-1}$)	A_C ($Jkg^{1/2}K^{-1}mol^{-3/2}$)	B_C (J kg $K^{-1}mol^{-2}$)	k_{23}^C (J kg $K^{-1}mol^{-2}$)
10	-336.9 ± 9	28.446	27.8 ± 4	46.8 ± 19
25	-179.4 ± 13	32.783	42.0 ± 5	-55.4 ± 26
25 Alfa	-189.5 ± 17	32.783	42.0 ± 5	-55.4 ± 26
40	-116.6 ± 7	37.446	54.7 ± 3	-109.9 ± 14
55	-72.3 ± 14	42.699	66.2 ± 5	-116.5 ± 28

* reported $\pm$ values are the standard deviations derived from the fits with unconstrained values of the $\bar{Y}^{\circ}$, B_Y, and k_{23}^Y parameters:

$$B_V(10 - 55°C) = -75.82 + 0.5247T - 0.0009123T^2$$
$$k_{23}^V(10 - 55°C) = 1208.3 - 8.010T + 0.01320T^2$$

$$B_C(10 - 55°C) = -480.47 + 2.610T - 0.002876T^2$$
$$k_{23}^C(10 - 55°C) = 10943 - 68.56T + 0.1062T^2$$

$$T/K = t/°C + 273.15$$

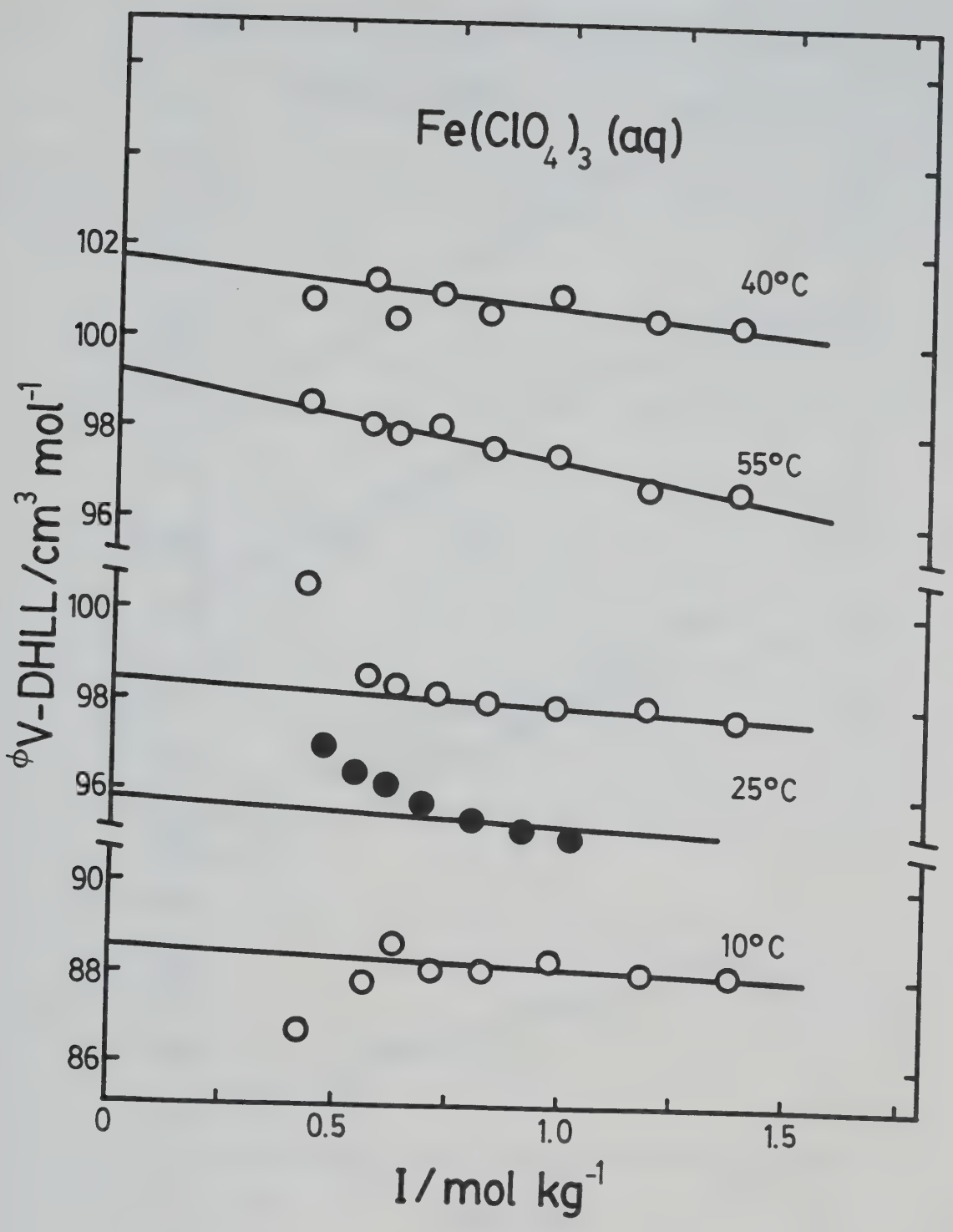

Figure 9.1: Apparent molar volumes of $Fe(ClO_4)_3(aq)$ minus the Debye-Hückel limiting law term (DHLL) as a function of ionic strength. The plotted curves are the result of fits using constrained values of the B_V and k_{23}^V parameters.

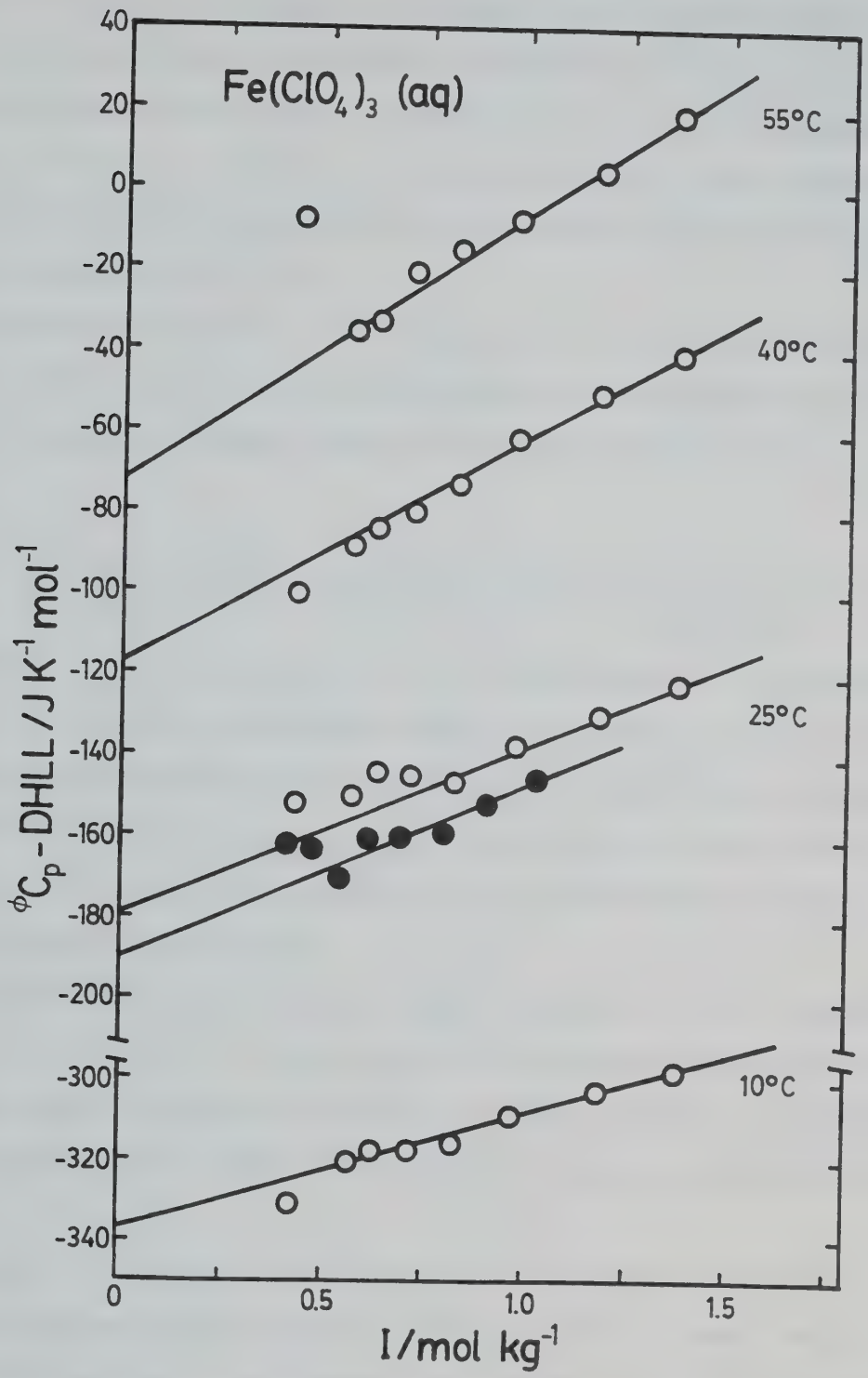

Figure 9.2: Apparent molar heat capacities of $Fe(ClO_4)_3(aq)$ minus the Debye-Hückel limiting law term (DHLL) as a function of ionic strength. The plotted curves are the result of fits using constrained values of the B_C and k_{23}^C parameters.

Ferrous perchlorate

Problems associated with analysis of the experimental apparent molar properties for ferric perchlorate solutions are of smaller magnitude for solutions containing ferrous perchlorate because much smaller concentrations of acid were required to prevent hydrolysis of $Fe^{2+}(aq)$. However, as mentioned earlier, these solutions have the additional (but minor) complication of small amounts of $Fe^{3+}(aq)$ formed as a result of the slow oxidation of $Fe^{2+}(aq)$.

The experimental apparent molar properties of solutions containing ferrous perchlorate, perchloric acid, and ferric perchlorate can be expressed as a sum of terms representing each of the three solutes as was done above for solutions of ferric perchlorate:

$$^{\phi}Y^{exptl} = \frac{m_2}{m_2+m_3+m_4}{}^{\phi}Y_2 + \frac{m_3}{m_2+m_3+m_4}{}^{\phi}Y_3 + \frac{m_4}{m_2+m_3+m_4}{}^{\phi}Y_4 + \delta \quad (9.13)$$

Here ${}^{\phi}Y_2$, ${}^{\phi}Y_3$, and ${}^{\phi}Y_4$ all apply at the total ionic strength of the solution, m_2, m_3, and m_4 are the equilibrium molalities of $Fe(ClO_4)_2$, $HClO_4$, and $Fe(ClO_4)_3$, and δ is an excess mixing term arising from interactions of all combinations of ions. Because m_2 is much larger than $(m_3 + m_4)$ and because the perchlorate anion is common to all three electrolytes, it is expected that the magnitude of δ is small enough to ignore in subsequent calculations.

The dependence of the apparent molar volumes and heat capacities of these solutions are assumed to be well represented by extended Debye-Hückel equations of the type given by eqs. 9.6 and 9.8-9.11. Again the values for the Debye-Hückel limiting slopes (A_Y) were taken from Ananthaswamy and Atkinson and are listed in Table 9.3.

Expressions of the type given by eqs. 9.6 and 9.8-9.11 were fitted to the experimental apparent molar properties listed in Table 9.2, using auxiliary data for perchloric acid and ferric perchlorate from Chapter 4 and Table 9.3, respectively. The temperature dependences of the B_Y and C_Y parameters were well represented by equations of type 9.12. Table 9.4 lists all of the smoothed values for the B and C terms and values for the standard state properties of $Fe(ClO_4)_2(aq)$.

Plots of ${}^{\phi}Y_2$ minus the Guggenheim form of the Debye-Hückel limiting law (shown

Table 9.4: Standard state partial molar volumes, heat capacities, and ionic strength parameters for $Fe(ClO_4)_2(aq)$.*

t (°C)	${}^{\phi}V_2^{\circ}$ ($cm^3 mol^{-1}$)	B_V ($cm^3 kg\ mol^{-2}$)	C_V ($cm^3 kg^{3/2} mol^{-5/2}$)
10	60.74 ± 0.18	0.379 ± 0.71	0.425 ± 0.51
25	66.00 ± 0.06	-0.065 ± 0.25	0.299 ± 0.17
40	71.80 ± 0.21	-5.317 ± 0.83	3.206 ± 0.59
55	76.55 ± 2.2	-15.38 ± 8.9	9.146 ± 6.3

t (°C)	${}^{\phi}C_{p,2}^{\circ}$ ($JK^{-1} mol^{-1}$)	B_C ($J\ kg\ K^{-1} mol^{-2}$)	C_C ($J\ kg^{3/2} K^{-1} mol^{-5/2}$)
10	-154.9 ± 0.8	30.04 ± 3.1	0.765 ± 2.2
25	-77.9 ± 1.0	14.09 ± 4.0	-1.557 ± 2.8
40	-34.7 ± 1.9	-19.81 ± 5.4	13.43 ± 5.4
55	-16.6 ± 10	-71.66 ± 40	45.73 ± 28

* Reported $\pm$ values are estimates of standard deviations from the fits with unconstrained ${}^{\phi}Y^{\circ}$, B_Y, and C_Y parameters.

$$B_V(10 - 55°C) = -893.090 + 6.1803T - 0.010683T^2$$
$$C_V(10 - 55°C) = 571.794 - 3.9263T + 0.00674T^2$$

$$B_C(10 - 55°C) = -3037.10 + 22.129T - 0.039897T^2$$
$$C_C(10 - 55°C) = 3291.77 - 22.514T + 0.038464T^2$$

$$T/K = t/°C + 273.15$$

in eq. 9.8) are given in Figures 9.3 and 9.4 for the calculated apparent molar properties of $Fe(ClO_4)_2(aq)$.

9.4 Discussion

9.4.1 Standard state properties

It is convenient to compare the present results with results from past work by converting the standard state volumes and heat capacities for salts into conventional ionic partial molar properties for the constituent ions. These conventional ionic partial molar properties are based on the useful convention $\bar{Y}^\circ(H^+, aq) \equiv 0$. The desired conventional $\bar{Y}^\circ$ values for $ClO_4^-(aq)$ are obtained directly from the properties of perchloric acid that were reported in Chapter 4. These values have been combined with the properties reported in Tables 9.3 and 9.4 for ferric and ferrous perchlorates to obtain the conventional properties for $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ that are listed in Table 9.5.

MILLERO (1972) cites values for the standard state partial molar volumes of $FeCl_3$ (24.0 cm^3mol^{-1}) and $Fe(NO_3)_3$ (49.7 and 36.5 cm^3mol^{-1}) at 25°C. These results can be combined with the standard state values $\bar{V}^\circ(Cl^-, aq) = 17.89$ cm^3mol^{-1} from ALLRED and WOOLLEY (1981) and $\bar{V}^\circ(NO_3^-, aq) = 29.32$ cm^3mol^{-1} (Chapter 2) to generate the values -29.7, -38.3, and -51.5 cm^3mol^{-1} for $\bar{V}^\circ(Fe^{3+}, aq)$. These results are in poor agreement with the present value, -33.7 cm^3mol^{-1}, listed in Table 9.5. Measurements of densities of solutions of ferric perchlorate in dilute perchloric acid by SWADDLE and MAK (1983) have led them to $\bar{V}^\circ[Fe(ClO_4)_3, aq] = 95.9 \pm 0.5$ cm^3mol^{-1}. This value is in excellent agreement with $\bar{V}^\circ[Fe(ClO_4)_3, aq] = 95.8$ cm^3mol^{-1} from solutions prepared from the Alfa sample, but is in less good agreement with $\bar{V}^\circ[Fe(ClO_4)_3, aq] = 98.4$ cm^3mol^{-1} from solutions prepared from the Strem sample. Recalculation of the data from SWADDLE and MAK (1983) with the present scheme (including the excess parameter) leads us to the value $\bar{V}^\circ[Fe(ClO_4)_3, aq] = 97.3 \pm 0.5$ cm^3mol^{-1} that is better agreement with the result based on solutions prepared with the sample from Strem.

Apparent molar heat capacities of ferric nitrate solutions reported by MYASNIKOVA *et al.* (1968) are the only results of sufficient precision for aqueous solutions

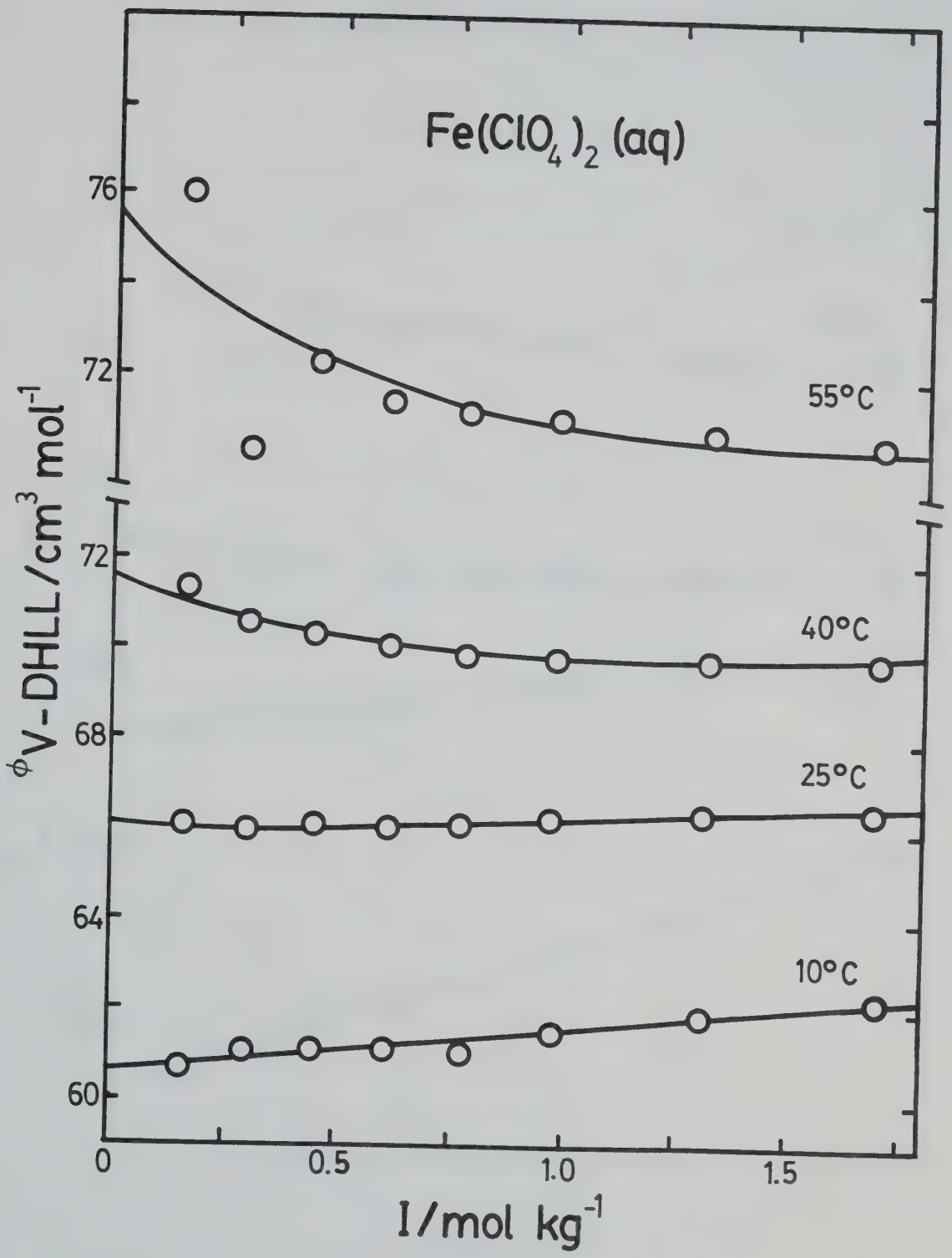

Figure 9.3: Apparent molar volumes of $Fe(ClO_4)_2(aq)$ minus the Debye-Hückel limiting law term (DHLL) as a function of ionic strength. The plotted curves are the result of fits using constrained values of the B_V and C_V parameters.

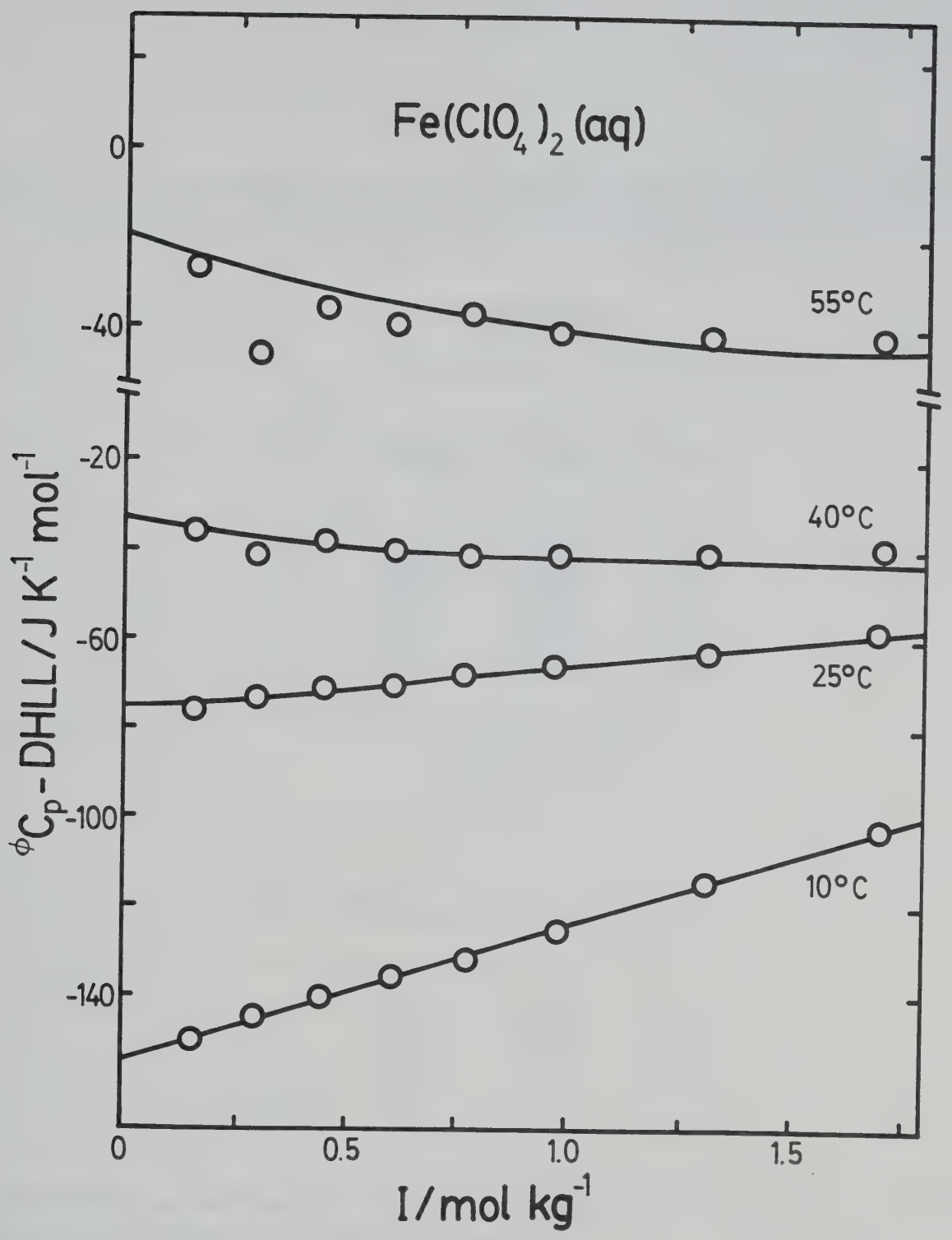

Figure 9.4: Apparent molar heat capacities of $Fe(ClO_4)_2(aq)$ minus the Debye-Hückel limiting law term (DHLL) (eq. 9.8) as a function of ionic strength. The plotted curves are the result of fits using constrained values of the B_C and C_C parameters.

Table 9.5: Conventional ionic partial molar volumes and heat capacities for $ClO_4^-(aq)$, $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ from 10 to 55°C based on $\bar{Y}°(H^+, aq) \equiv 0$.*

	$\bar{V}°/(cm^3mol^{-1})$		
t (°C)	$ClO_4^-(aq)$	$Fe^{2+}(aq)$	$Fe^{3+}(aq)$
10	41.63	−22.52	−36.4
25	44.04	−22.08	−33.7
40	46.24	−20.68	−37.0
55	47.31	−18.07	−42.74
	$\bar{C}_p°/(JK^{-1}mol^{-1})$		
t (°C)	$ClO_4^-(aq)$	$Fe^{2+}(aq)$	$Fe^{3+}(aq)$
10	−62.2	−30.5	−150.3
25	−25.0	−27.9	−104.4
40	−9.0	−16.7	−89.6
55	−5.2	−6.2	−56.7

* All results reported here for $Fe^{3+}(aq)$ were generated using data obtained from the Strem sample of ferric perchlorate hexahydrate.

containing iron(III) to permit useful comparisons with the present results. They have derived $\bar{C}_p^\circ[Fe(NO_3)_3, aq]$ = -402 J $K^{-1}mol^{-1}$ at 25°C. Combination of this value with $\bar{C}_p^\circ(NO_3^-, aq)$ = -71.6 J $K^{-1}mol^{-1}$ from Chapter 2 leads to $\bar{C}_p^\circ(Fe^{3+}, aq)$ = -187 J $K^{-1}mol^{-1}$, in poor agreement with the present $\bar{C}_p^\circ(Fe^{3+}, aq)$ = -104 J $K^{-1}mol^{-1}$. This difference is almost certainly due to the lack of consideration of hydrolysis reactions in the study by MYASNIKOVA *et al.* (1968). It is believed that the present results are the most reliable because of the consideration of hydrolysis and other complicating factors.

Millero's review (MILLERO, 1972) lists $\bar{V}^\circ(FeCl_2)$ = 13.8 and 18.0 and $\bar{V}^\circ(FeBr_2)$ = 23.0 cm^3mol^{-1}, all referring to 25°C. These results can be combined with the conventional ionic volumes of Cl^-(aq) cited above and $\bar{V}^\circ(Br^-, aq)$ = 24.71 cm^3mol^{-1} from MILLERO (1972) to derive -22.0, -17.8, and -26.4 cm^3mol^{-1} for Fe^{2+}(aq). The first value is in exact agreement with the present $\bar{V}^\circ(Fe^{2+}, aq)$ = -22.08 cm^3mol^{-1}. Difficulties in the handling of aqueous solutions containing ferrous ion are probably partly responsible for the scatter among previous results. Again it is believed that the present results are the most accurate presently available.

Measurements of heat capacities of aqueous solutions containing ferrous chloride have led to $\bar{C}_p^\circ(FeCl_2, aq)$ = -289 J $K^{-1}mol^{-1}$ at 25°C from KARAPET'YANTS *et al.* (1977), and measurements from WOOD *et al.* (1988) at 17.9 MPa have been extrapolated (out of the region where these results were obtained, 76 to 324°C) to obtain $\bar{C}_p^\circ(FeCl_2, aq)$ = -240 J $K^{-1}mol^{-1}$ at 25°C. Estimates of pressure effects on standard state heat capacities from WHITE *et al.* (1987) for $CaCl_2$, has lead to $\bar{C}_p^\circ(FeCl_2, aq)$ = -251 J $K^{-1}mol^{-1}$ at 25°C and 0.1 MPa. These results were combined with $\bar{C}_p^\circ(Cl^-, aq)$ = -126.6 J $K^{-1}mol^{-1}$ from TREMAINE *et al.* (1986) to derive $\bar{C}_p^\circ(Fe^{2+}, aq)$ = -36 and 2 J $K^{-1}mol^{-1}$. The former result is in good agreement and the latter result is in fair agreement with the present $\bar{C}_p^\circ(Fe^{2+}, aq)$ = -28 J $K^{-1}mol^{-1}$.

Integral heats of dilution and heat capacities of concentrated solutions of $FeCl_2$ have also been measured from 15 to 35°C (BERNADUCCI *et al.*, 1979). These measurements led to the value $\bar{C}_p^\circ(Fe^{2+}, aq)$ = -2 ± 30 J $K^{-1}mol^{-1}$ at 25°C, that can be compared with the present value of $\bar{C}_p^\circ(Fe^{2+}, aq)$ = -28 J $K^{-1}mol^{-1}$. This latter result is in good agreement with our value especially considering their narrow

temperature range of study.

It is believed that all of the results listed in Table 9.6 are the best currently available for ferrous and ferric ion over the stated temperature range. *Total* uncertainties in the standard state volume and heat capacities are about ± 2 cm^3mol^{-1} and ± 15 J $K^{-1}mol^{-1}$ for Fe^{3+}(aq) and ± 0.4 cm^3mol^{-1} and ± 4 J $K^{-1}mol^{-1}$ for Fe^{2+}(aq) from 10 to 40°C, and slightly larger uncertainties at 55°C.

Representations from 10 to 55°C

Following procedures described in earlier chapters, modified versions of the equation suggested by HOLMES and MESMER (1983) were used to represent the temperature dependence of the standard state heat capacities and volumes of $Fe(ClO_4)_3$ and $Fe(ClO_4)_2$:

$$\bar{Y}_2^\circ = a + \frac{b}{T-\theta} + cT + dT^2 \tag{9.14}$$

Equations of type eq. 9.14 were fitted to the data given in Tables 9.3 and 9.4 to obtain the following expressions valid over the present temperature range:

$$\bar{V}^\circ[Fe(ClO_4)_3,\ aq) = -1258.5 + 8.6584T - 0.013778T^2 \tag{9.15}$$

$$\bar{C}_p^\circ[Fe(ClO_4)_3,\ aq) = 4233.0 - \frac{189340}{T-190} - 8.9529T \tag{9.16}$$

$$\bar{V}^\circ[Fe(ClO_4)_2,\ aq) = -75.95 + 0.59157T - 0.00038554T^2 \tag{9.17}$$

$$\bar{C}_p^\circ[Fe(ClO_4)_2,\ aq) = 2128.1 - \frac{96384}{T-190} - 4.4089T \tag{9.18}$$

Plots based on these equations are shown along with the experimental data for $Fe(ClO_4)_3$ and $Fe(ClO_4)_2$ in Figures 9.5 through 9.8.

In Chapter 4 expressions that describe the temperature dependence of the standard state heat capacities of $HClO_4$(aq) from 10 to 55 °C and the standard state volumes from 10 to 65 °C were reported:

$$\bar{V}^\circ(HClO_4,\ aq) = -107.79 + 0.87322T - 0.0012203T^2 \tag{9.19}$$

$$\bar{C}_p^\circ(HClO_4,\ aq) = 1408.1 - \frac{55801}{T-190} - 3.0767T \tag{9.20}$$

Combination of the equations for ferric and ferrous perchlorate with equations for perchloric acid lead to the following equations valid from 10 to 55°C :

$$\bar{V}^\circ(Fe^{3+},\ aq) = -935.1 + 6.0387T - 0.010117T^2 \tag{9.21}$$

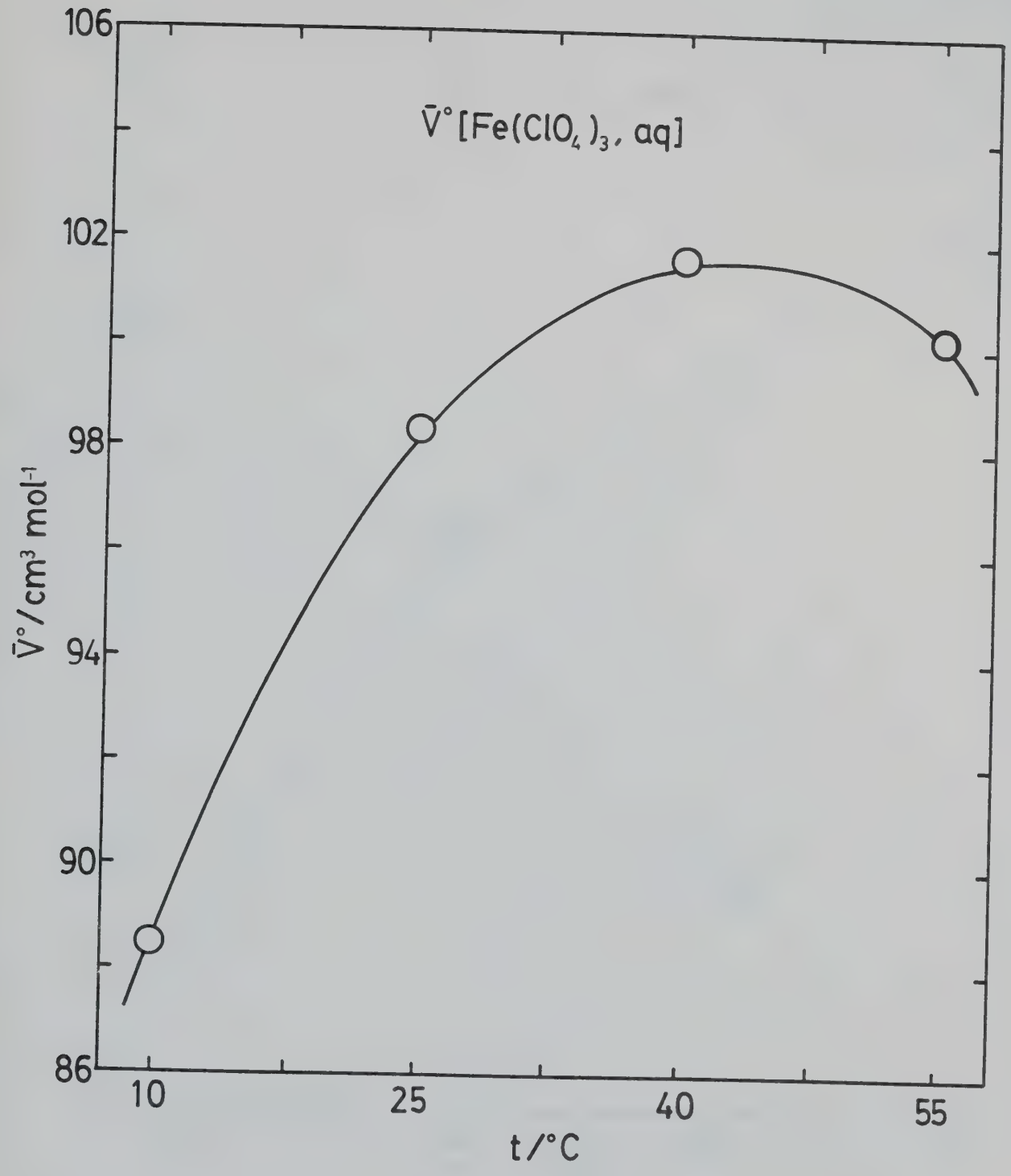

Figure 9.5: Standard state partial molar volumes for $Fe(ClO_4)_3(aq)$. The solid line is the fit according to eq. 9.15.

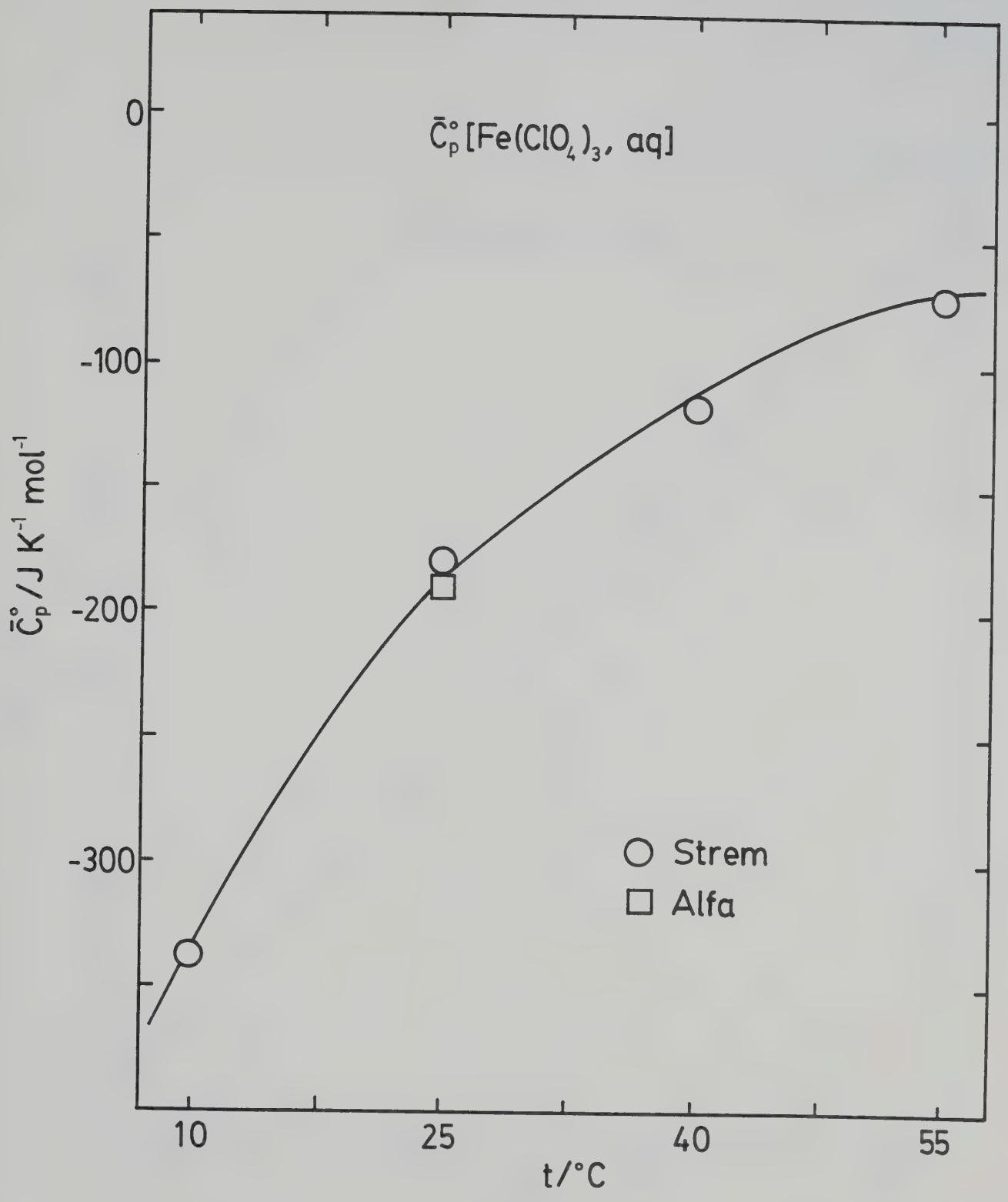

Figure 9.6: Standard state partial molar heat capacities for $Fe(ClO_4)_3(aq)$. The solid line is the fit according to eq. 9.16

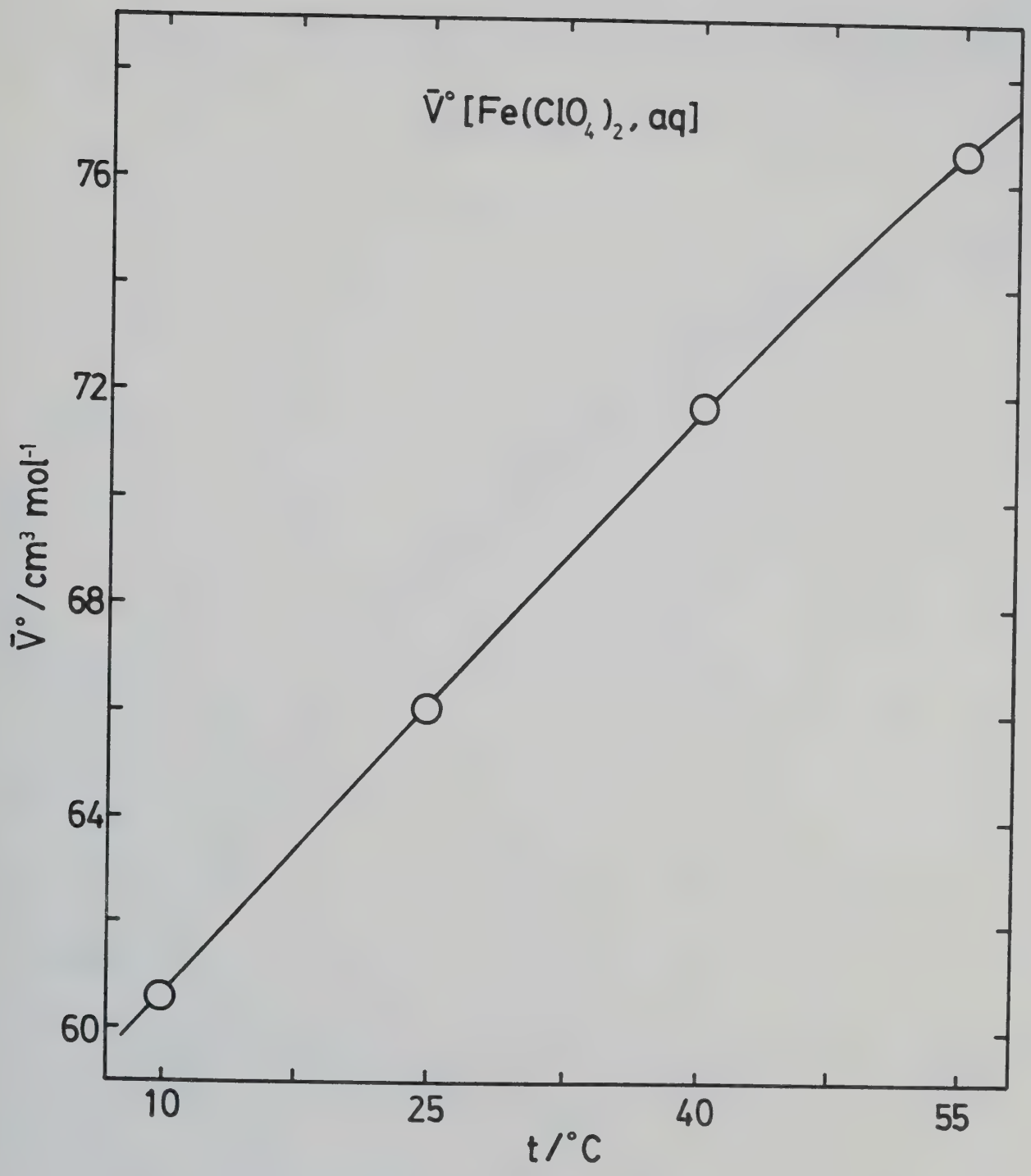

Figure 9.7: Standard state partial molar volumes for $Fe(ClO_4)_2$(aq). The solid line is the fit according to eq. 9.17.

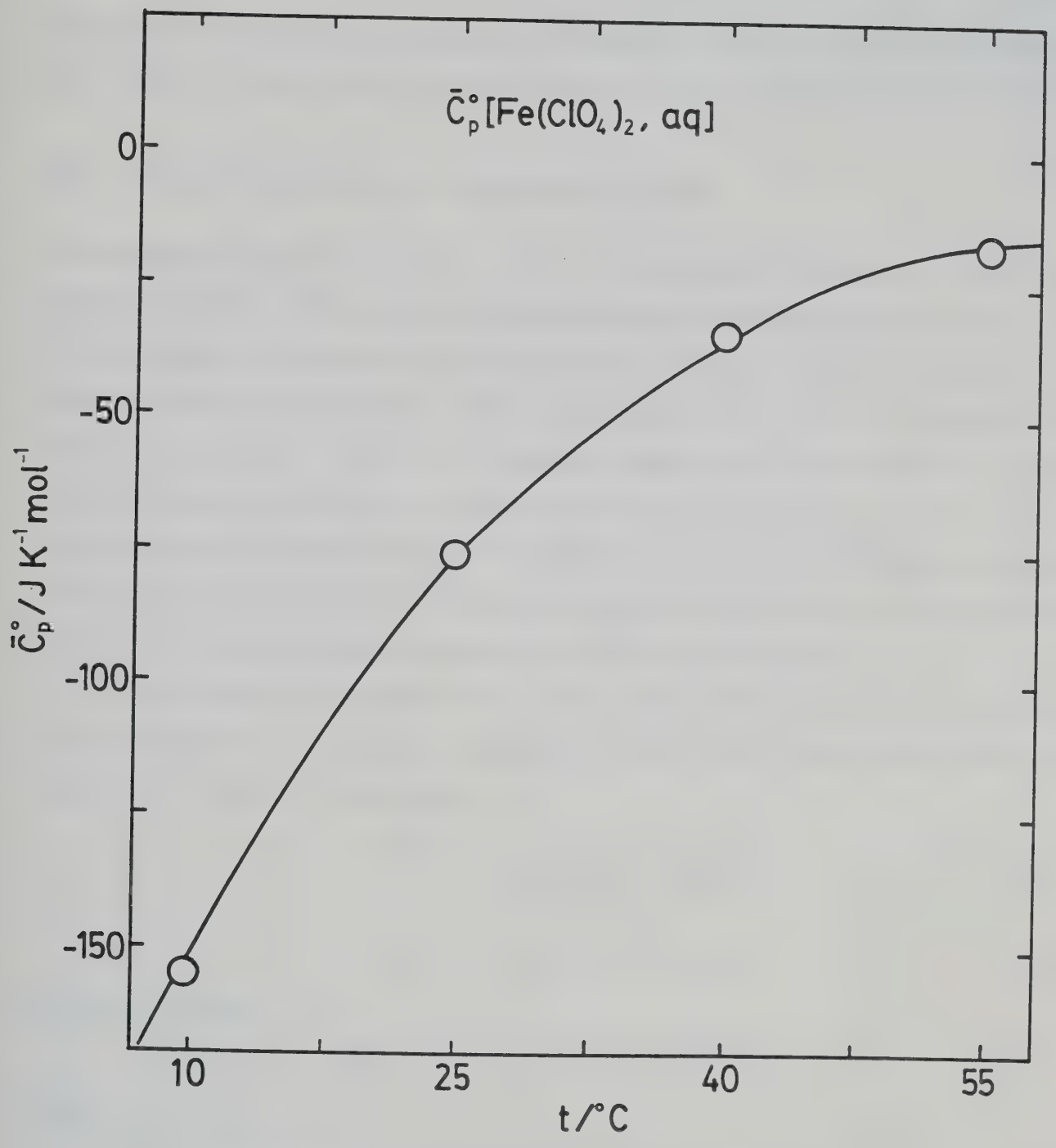

Figure 9.8: Standard state partial molar heat capacities for $Fe(ClO_4)_2(aq)$. The solid line is the fit according to eq. 9.18

$$\bar{C}_p^\circ(Fe^{3+},\ aq) = 8.7 - \frac{21937}{T-190} + 0.2772T \quad (9.22)$$

$$\bar{V}^\circ(Fe^{2+},\ aq) = 139.63 - 1.1549T + 0.0020551T^2 \quad (9.23)$$

$$\bar{C}_p^\circ(Fe^{2+},\ aq) = -688.1 + \frac{15218}{T-190} + 1.7445T \quad (9.24)$$

For calculations involving temperatures from 10 to 55°C, the functions presented above should be used rather than the high temperature estimations derived below.

9.5 High temperature extrapolations

As discussed in detail in Chapter 4, and as illustrated in Chapters 4, 7, and 8, the Helgeson-Kirkham-Flowers(HKF) semi-theoretical representation of standard state thermodynamic properties of aqueous ions is an excellent means by which low temperature thermodynamic data (such as investigated here) can be extrapolated to higher temperatures. There are numerous reasons why thermodynamic data for aqueous species are required at high temperatures as mentioned in the Introduction to this Chapter and several others. Because of the experimental difficulties associated with high temperature measurements, the approach described and demonstrated below has proven to be a useful alternative to direct measurement.

The HKF model (HELGESON *et al.*, 1981) gives the following functional forms for the temperature dependence of standard state partial molar volumes and heat capacities of aqueous electrolytes:

$$\bar{V}^\circ = \sigma + \frac{\xi T}{T-\theta} + \Delta V_{BORN} \quad (9.25)$$

$$\bar{C}_p^\circ = c_1 + \frac{c_2 T}{T-\theta} + \Delta C_{p,BORN} \quad (9.26)$$

In these equations

$$\Delta V_{BORN} = -\omega Q = -\omega \frac{1}{\epsilon}\left(\frac{\partial \ln \epsilon}{\partial p}\right)_T \quad (9.27)$$

and

$$\Delta C_{p,BORN} = \omega T X = \omega T \frac{1}{\epsilon}\left[\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_p - \left(\frac{\partial \ln \epsilon}{\partial T}\right)_p^2\right] \quad (9.28)$$

Expressions of these types were fitted to the standard state partial molar volumes and heat capacities listed in Tables 9.4 and 9.5. In all of these equations the "effective" radii for anionic species are equivalent to crystallographic radii, and for cationic

species they are equal to crystallographic radii plus 0.94 Å. These effective aqueous radii were calculated from the "effective ionic radii" listed by SHANNON (1976). Values of X and Q were taken from the compilations of HELGESON and KIRKHAM (1974, 1976). The results of the HKF fits to the experimental results reported here, and also the fits to data for $HClO_4$(aq) (required in subsequent calculations) are as follows:

$$\frac{\bar{V}^\circ[Fe(ClO_4)_3,\ aq]}{cm^3mol^{-1}} = 138.43 - \frac{4.658T}{T-245} - 25.539 \times 10^6 Q \tag{9.29}$$

$$\frac{\bar{C}_p^\circ[Fe(ClO_4)_3,\ aq]}{J\ K^{-1}mol^{-1}} = 573.47 - \frac{92.6442T}{T-245} - 25.539 \times 10^5 TX \tag{9.30}$$

$$\frac{\bar{V}^\circ[Fe(ClO_4)_2,\ aq]}{cm^3mol^{-1}} = 102.509 - \frac{4.8374T}{T-243} - 15.444 \times 10^6 Q \tag{9.31}$$

$$\frac{\bar{C}_p^\circ[Fe(ClO_4)_2,\ aq]}{J\ K^{-1}mol^{-1}} = 361.21 - \frac{54.1683T}{T-243} - 15.444 \times 10^5 TX \tag{9.32}$$

$$\frac{\bar{V}^\circ[HClO_4,\ aq]}{cm^3mol^{-1}} = 84.508 - \frac{16.465T}{T-167.4} - 4.75415 \times 10^6 Q \tag{9.33}$$

$$\frac{\bar{C}_p^\circ[HClO_4,\ aq]}{J\ K^{-1}mol^{-1}} = 89.43 - \frac{8.6367T}{T-261.0} - 4.75415 \times 10^5 TX \tag{9.34}$$

As can be seen by the above equations, the θ values for the volume and heat capacity fits were constrained to be the same for ferrous and ferric perchlorate salts but not for perchloric acid. It was found that the volumetric data for the iron systems did not adequately establish these θ values (not uncommon). Fitting equations of this type to experimental data (with only four data points) can lead to convergence problems because of the nature of the fits. Therefore, the θ values were determined solely from the fits to the heat capacity data that were then used in the fits to the volumetric data.[1]

9.5.1 Standard potential of the ferric-ferrous ion couple to 300°C

There are several applications that require data or would benefit from the knowledge of the standard electrode potential of the ferric-ferrous couple to high temperatures. One specific illustration arises in connection with solubilities of sparingly soluble oxides such as magnetite (BAES and MESMER, 1976; TREMAINE and LEBLANC,

[1] Fitting results with the HKF model is supposed to result in the same values of θ for heat capacities and volumes. Practice has shown this not always to be the case (Chapters 4 and 7).

1980). The HKF expressions reported above can be used to calculate high temperature Gibbs free energies for $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ that can then be used to evaluate the standard electrode potential of the ferric-ferrous couple at high temperatures.

The Gibbs free energy is related to heat capacities and volumes by the following expressions

$$\left(\frac{\partial \Delta G^\circ}{\partial T}\right)_p = -\Delta S^\circ \tag{9.35}$$

$$\left(\frac{\partial \Delta S^\circ}{\partial T}\right)_p = \frac{\Delta C_p^\circ}{T} \tag{9.36}$$

$$\left(\frac{\partial \Delta G^\circ}{\partial p}\right)_T = \Delta V^\circ \tag{9.37}$$

Based on these equations, calculations of the Gibbs free energy of formation of a species over a range of temperatures and pressures, referenced to the elements in their standard states at 298.15 K and 1 bar are done using

$$\Delta G_T^\circ = \Delta G_{f,298}^\circ - \bar{S}_{298}^\circ(T - 298.15) + \int_{298}^{T} \bar{C}_p^\circ dT - T\int_{298}^{T} \frac{\bar{C}_p^\circ}{T} dT + \int_1^p \bar{V}^\circ dp \tag{9.38}$$

where $\bar{S}_{298}^\circ$ is equal to the standard state partial molar entropy of the species at 298.15 K and 1 bar.

The reaction of present interest can be represented by

$$Fe^{3+}(aq) + \frac{1}{2}H_2(g) = Fe^{2+}(aq) + H^+(aq) \tag{9.39}$$

In order to calculate ΔG° and thence the standard potential for reaction 9.39, extrapolated values for the Gibbs free energy of formation for each of the participating species must be evaluated. Because of the relative uncertainties in the room temperature thermodynamic properties of ferrous and ferric ions, it is not appropriate here to simply take the required room temperature entropies and Gibbs free energies from the compilation by WAGMAN *et al.* (1982). Results of calculations using eq. 9.38 are summarized following the next section.

Selections of thermodynamic values

As mentioned several times earlier, there are discrepancies in the existing thermodynamic data for many species in the iron-water system. Because of these uncertainties

it is appropriate here to suggest our estimated "best" values and then use these values in subsequent calculations in this section. The choices made here can easily be revised should new (better) results become available.

It is now generally accepted that the best cycle that can be used to select "best" values for aqueous ferrous and ferric cations comes from LARSON *et al.* (1968). The standard state entropy value for Fe^{2+}(aq) determined from LARSON *et al.* (1968) is -107.1 J $K^{-1}mol^{-1}$, based on accurate calorimetric and solubility results. It is believed that the more recent heat of solutions results for ferrous chloride (CERUTTI and HEPLER, 1977) are the "best" available for a ferrous salt. They report $\Delta H^{\circ}_{f,298}(Fe^{2+}, aq) = -90.42$ kJ mol^{-1} from these measurements. This value is combined with the standard state entropy and auxiliary data from the NBS tables (WAGMAN *et al.*, 1982) to derive $\Delta G^{\circ}_{f,298}(Fe^{2+}, aq) = -89.32$ kJ mol^{-1}. All of these values refer to 298.15 K.

Values of these same quantities can be derived for ferric ion by referencing accurate electrochemical and calorimetric results to the data above. Accurate standard electrode potentials for the reactions represented by eq. 9.39 are available at T=298.15 K (BRAY and HERSHEY, 1934; MATTOO, 1960; SCHUMB *et al.*, 1937; LATIMER, 1952; HEUSLER and LORENZ; 1985) and also over a narrow range of temperatures near T=298 K (WHITTEMORE and LANGMUIR, 1972). All of these results are in good agreement, and the value $E^{\circ}_{298} = 0.770$ V was selected. Standard electrode potentials are related to the changes in the Gibbs free energy of a reaction by the fundamental equation

$$\Delta G^{\circ} = n\mathcal{F}E^{\circ}_{298} \tag{9.40}$$

where $\mathcal{F}$ is the Faraday (96487 kJ $mol^{-1}V^{-1}$) and n is the number of moles of electrons involved in the reaction (in this case one). This selected standard potential, in combination with auxiliary data from the NBS tables, and the selected properties for ferrous ion listed above, leads to $\Delta G^{\circ}_{f,298}(Fe^{3+}, aq) = -15.0$ kJ mol^{-1}. LARSON *et al.* (1968) have suggested the value $\Delta H^{\circ} = -42 \pm 2$ kJ mol^{-1} for reaction 9.39. Temperature dependent standard electrode potentials from WHITTEMORE and LANGMUIR (1972) have resulted in an enthalpy change of -42.7 ± 1.7 kJ mol^{-1} consistent with the recommendations of LARSON *et al.* (1968). This latter value was selected and combined with auxiliary data from the NBS tables to generate $\Delta H^{\circ}_{f,298}(Fe^{3+}, aq) =$

-47.7 kJ mol^{-1}. This value was combined with auxiliary data and the $\Delta G^{\circ}_{f,298}$ value for ferric ion to obtain the $\bar{S}^{\circ}_{298}(Fe^{3+}, aq) = -278.4$ J K^{-1}mol^{-1}. All of these values are listed in Table 9.7 along with some auxiliary data.

9.5.2 Calculations

The thermodynamic properties associated with reaction 9.39 can be calculated by the following scheme:

$$Fe(ClO_4)_3(aq) + \frac{1}{2}H_2(g) = Fe(ClO_4)_2(aq) + HClO_4(aq) \qquad (9.41)$$

High temperature Gibbs free energies were calculated as described above [using room temperature data from Table 9.6, and the heat capacity expression for $H_2(g)$ from KELLEY (1960)] and combined with eq. 9.40 to generate values of the standard electrode potential for the ferrous-ferric ion couple to 300°C. The results of these calculations are shown along with experimental data to 35°C in Figure 9.9 and in Table 9.7. Experience has demonstrated (Chapters 4, 7, and 8) that these calculations should be within experimental error to 200°C and since no other data are presently available, they should be used at higher temperatures (with caution) until more direct results become available. The present calculations of the standard electrode potential of the ferric-ferrous ion couple represent the most demanding application of the present data since the high temperature Gibbs free energies were calculated from data presented here and in Chapter 4 for all but one of the species [that for $H_2(g)$]. Values of the standard potentials for the reduction of both ferrous and ferric ion to iron metal can be calculated from the present results using auxiliary data for iron metal. These latter calculations are of much interest but are not presented here because of the similarity of these calculations to those just presented. The present heat capacity and volume results can be used to refine some low temperature thermodynamic properties for species in the iron system. These and other calculations are in progress.[2]

[2] J.K. Hovey and L.G. Hepler

Table 9.6: Selected thermodynamic values at 25°C.

Species	$\Delta G^\circ_{f,298}$ (kJ mol^{-1})	$\bar{S}^\circ_{298}$ (J K^{-1}mol^{-1})
$H^+(aq)$	0	0
$H_2(g)$	0	130.684
$Fe^{3+}(aq)$	−15.0	−278.4
$Fe^{2+}(aq)$	−89.32	−107.1
$ClO_4^-(aq)$	−8.52	182.0

Table 9.7: Calculated standard electrode potentials for the ferric-ferrous ion couple $[Fe^{3+}(aq) + \frac{1}{2}H_2(g) = Fe^{2+}(aq) + H^+(aq)]$ to 300°C.

t (°C)	$E°$ (V)
0	0.743
25	(0.770)*
50	0.798
75	0.827
100	0.857
150	0.917
200	0.981
250	1.052
300	1.144

* Selected result (see text).

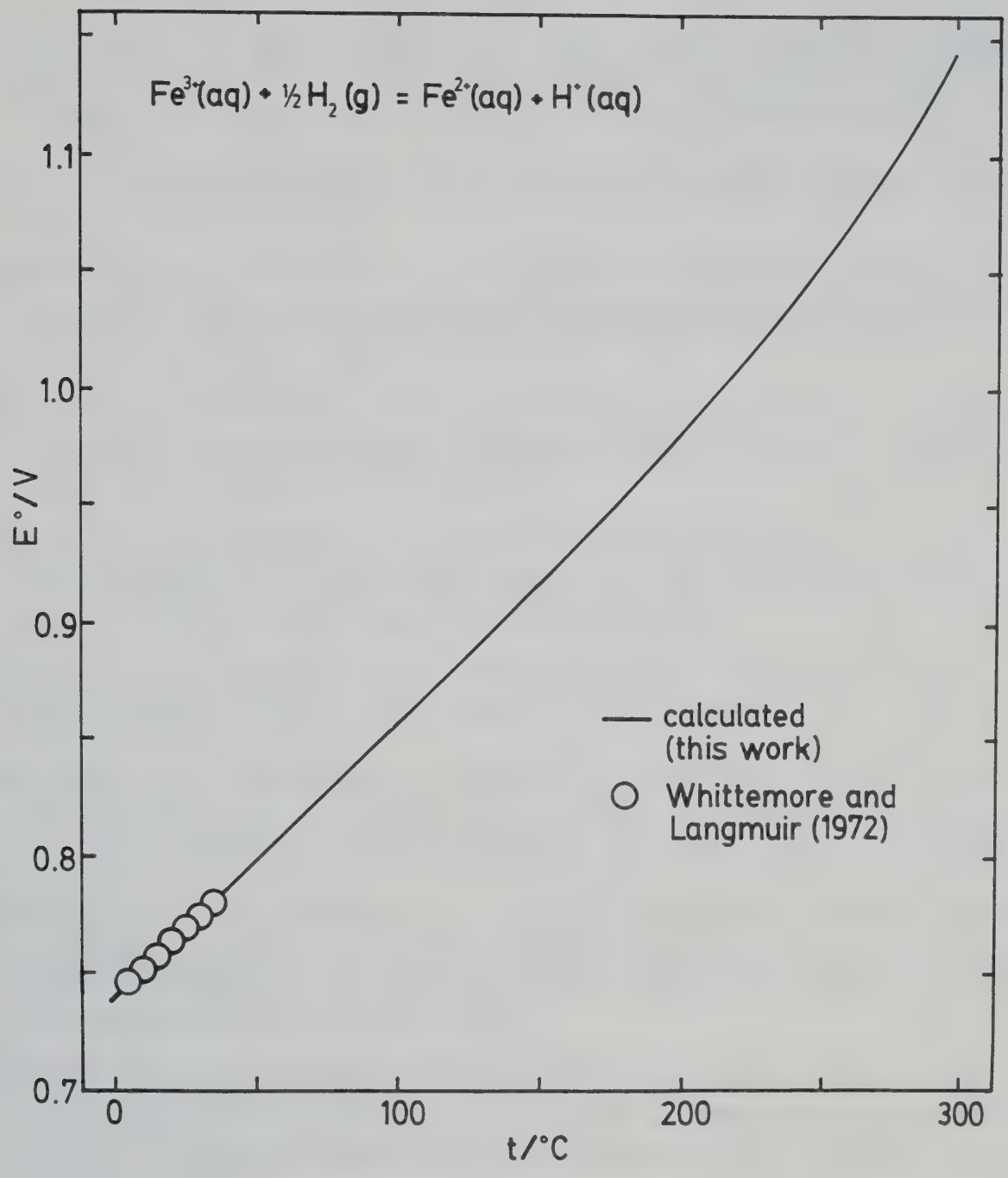

Figure 9.9: Predicted and experimental values of the standard electrode potential of the ferric-ferrous ion couple to 300°C.

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Chapter 10

Prediction of high temperature equilibrium properties for 3+ ions and their mononuclear hydrolyzed species to 300°C

10.1 Introduction

Numerous computer codes and thermodynamic data bases for aqueous species for use in modelling chemical equilibria in aqueous environments have been developed in recent years [see for example WOLERY (1983), KHARAKA *et al.* (1988), HELGESON *et al.* (1970), NORDSTROM and MUNOZ (1985), BALL *et al.* (1981)]. Many of the computer codes developed prior to 1979 have been extensively reviewed and compared by NORDSTROM *et al.* (1979). These codes mostly use data bases that refer specifically to $T = 298.15\ K$, supplemented by selected high temperature data. Because of the absence of required heat capacities of aqueous species (partly remedied by work in the present thesis), it has been necessary to use various correlations to predict missing properties. One such correlation is the entropy correspondence principle proposed by CRISS and COBBLE (1964a,b); this correlation has several advantages (see Chapter 3) but also some disadvantages (see Chapters 6 and 7).

In principle all of the needed thermodynamic properties that are now missing can be obtained directly by way of various measurements. But a principal practical value of thermodynamics is that one need not measure every property that is needed. Instead, one measures some properties and calculates (reliably) some other properties that are required. Choices as to which properties are measured and which properties are calculated are based on experimental convenience, efficiency (some measured properties can be used in several calculations), and accuracy. Many of the investigations described in this thesis have focussed on heat capacities of aqueous solutions and the derived partial molar heat capacities of solutes because these quantities can

be used in a large number of thermodynamic calculations.

Many of the thermodynamics properties of present interest have not yet been determined. Of these, some are clearly very difficult to determine. All of these considerations mean that we do not have many of the thermodynamic properties (including partial molar heat capacities that are of immediate interest) that are wanted and it is unlikely that all of the properties of interest will ever be measured. It is partly because of the absence of needed thermodynamic data that previous investigators have developed various correlations and predicitive schemes. Another reason for developing theory-based correlations is that comparison of the correlation scheme with known properties permits testing and evaluation of the underlying theory. Finally, it should be recognized that even theoretical correlations later proven unsatisfactory can be a useful aid in selecting important systems for experimental investigations.

Of particular interest in this context are the thermodynamic properties (Gibbs free energies, enthalpies, entropies, heat capacities) of aqueous metal ions and associated hydrolyzed species. The importance of these data at low and high temperatures has been discussed in Chapters 6 through 9. This present Chapter provides a method that can be used to predict the high temperature equilibrium properties for these types of species. The method is developed first for the aluminum-water system and is extended to the iron-water system.

10.2 Trivalent metal ion hydrolysis–basic premise

The states of aqueous ions at room temperature (i.e. nature and number of coordinated water molecules) are available for a limited number of species. Several recent studies give methods and calculation procedures for the evaluation of coordination numbers of monatomic ions (KRISTIANSSON *et al.*, 1988; CAMINITI *et al.*, 1980; ALBRIGHT, 1972; LICHERI *et al.*, 1975). However, data are particularly lacking for complex or hydrolyzed species, mostly because of the difficulties associated with sparingly soluble species. The most common state of aqueous metal cations (especially transition metal ions) is a six-coordinate octahedral geometry. The hydrolysis of trivalent metal ions with octahedral geometry in aqueous solution may

be represented by

$$M(H_2O)_6^{3+} = MOH(H_2O)_5^{2+} + H^+ \qquad (10.1)$$

$$MOH(H_2O)_5^{2+} = M(OH)_2(H_2O)_4^{+} + H^+ \qquad (10.2)$$

$$\vdots$$

$$M(OH)_3(H_2O)_x = M(OH)_4^{-} + (x-1)H_2O + H^+ \qquad (10.3)$$

A preliminary approach to a description of these hydrolysis equilibria is to assume that differences in the thermodynamic properties of the ions are due primarily to "structural" differences and that these differences may be assumed to vary in some orderly fashion from species of type $M^{3+}(aq)$ to those of type $M(OH)_4^-(aq)$. The exact number of coordinated water molecules on each ion in the present scheme is immaterial so long as the number changes in an "orderly" way from one ion in the scheme to the next. Deviations from "orderly" changes are most likely to occur starting with the formation of the neutral hydroxide.

It is expected that the thermodynamic property change associated with each "step" in the hydrolysis sequence is made up of several components. These components are supposed to involve changes due to the geometric expansion of the solute, changes in ion-water dipole interactions in the primary and secondary solvation spheres due to changes in both charge and ionic size, and changes in the number and nature of coordinated water molecules. Consideration of these effects requires consideration of the relationship between conventional and absolute thermodynamic properties of ions. It is expected that the structural effects do not vary linearly for the steps involving the non-ionic or electrically neutral solute species (as mentioned above).

The last component in the present approach is to assume that differences in the thermodynamic properties for neutral solutes can be accounted for by using thermodynamic properties for the boric acid-borate system. The standard state volumes and heat capacities of $B(OH)_3(aq)$ and $B(OH)_4^-(aq)$ that were presented in Chapter 8 will be used for this purpose, along with the known standard state entropies at 298.15 K. Results of these calculations will then be assumed to represent

the differences in thermodynamic properties for all species of the type $M(OH)_3(aq)$ and $M(OH)_4^-(aq)$.

10.3 Equation development

Since a basic premise behind the present model is that the purely "structural" changes for the ionic species vary in stepwise fashion, means of accounting for the other factors must be specified. All contributions to the observed differences in the thermodynamic properties will be labeled "structural" except those associated with the change in the electrostatic interactions of the solute with water dipoles at distances greater than the primary solvation sphere. These latter contributions that can be labeled "electrostatic" can be estimated to a first approximation by the classic equation proposed by BORN (1920) that considers ions to be hard spheres and water to be represented by its static dielectric constant. The thermodynamic differences in conventional ionic properties (entropies, volumes, heat capacities) are expected to vary linearly between $M^{3+}(aq)$ and $M(OH)_4^-(aq)$ [with the exception of $M(OH)_3$, as discussed earlier] once the "electrostatic" contributions have been subtracted.

10.3.1 Electrostatic model and equations. Standard state entropies

As discussed in Chapter 7, the only system for which standard state heat capacities and volumes are known for both the completely unhydrolyzed metal cation and the prevalent species in alkaline solution, is the aluminum system. Standard state entropies are also known for several of the intermediate hydrolyzed species. Heat capacity and volume results for this system will therefore be used to evaluate parameters for equations that will be used later.

The electrostatic contributions to the thermodynamic properties must first be subtracted to obtain the desired changes in the "structural" contributions. The Born terms are defined by

$$\Delta S_{Born} = \omega \frac{1}{\epsilon} \left(\frac{\partial \ln \epsilon}{\partial T} \right)_p \tag{10.4}$$

$$\Delta V_{Born} = -\omega \frac{1}{\epsilon} \left(\frac{\partial \ln \epsilon}{\partial p} \right)_T \tag{10.5}$$

$$\Delta C_{p,Born} = -\omega T \frac{1}{\epsilon}\left[\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_p - \left(\frac{\partial \ln \epsilon}{\partial T}\right)_p^2\right] \tag{10.6}$$

where ϵ is the static dielectric constant of water, ω is a constant multiplied by z^2/r_{eff} and r_{eff} is the "effective" radius of an ion in water. The present r_{eff} values (HELGESON *et al.*, 1981) were taken equal to crystallographic radii for anions and to be crystallographic radii plus 0.94 Å for cations using "effective ionic radii" from SHANNON (1976).

Since the present scheme will be derived in terms of conventional ionic properties [$\bar{Y}(H^+, aq) \equiv 0$], the ω term appropriate for the above equations is related to the ω value for hydrogen ion ($\omega_{H+} = 2.2554 \times 10^5$ J mol^{-1}) and ionic charge by

$$\omega/(\text{J mol}^{-1}) = 6.9466 \times 10^5 \frac{z^2}{r_{eff}} - z\omega_{H+} \tag{10.7}$$

The electrostatic contributions for the ions were estimated by using the appropriate quantities involving the dielectric constant of water and its pressure and temperature derivatives from HELGESON *et al.* (1974, 1976, 1981). Values of thermodynamic properties for several aqueous aluminum and hydrolyzed species are well known at 298.15 K, but several others are not known. A summary of the selected values at 298.15 K and the results of the present approach in terms of the standard state entropies of aluminum and its hydrolyzed species are presented below.

10.3.2 Selections of thermodynamic data

All of the selected and calculated values for the thermodynamic properties of $Al^{3+}(aq)$, $AlOH^{2+}(aq)$, $Al(OH)_2^+(aq)$, $Al(OH)_3(aq)$, and $Al(OH)_4^-(aq)$ are given in Table 10.1. Choices for the non-parenthesized values (experimental) listed in the table come from critical selections of the appropriate quantities from the literature as follows. From values for $\Delta G^\circ_{f,298}[Al^{3+}(aq)]$ (COUTURIER *et al.*, 1984; WAGMAN *et al.*, 1982; HEMINGWAY and ROBIE, 1977; APPS (in prep.); BERSILLON *et al.*, 1978; HEMINGWAY, 1982) the listed value was selected primarily from consideration of the data from COUTURIER *et al.* that is consistent with the selections of APPS and BERSILLON *et al.* but more positive than the selected value from HEMINGWAY. The calorimetric value of $\Delta H^\circ_{f,298}[Al^{3+}(aq)]$ from LATIMER and GREENSFELDER (1928) was chosen instead of values derived from $K = f(T)$ or values derived from other schemes

(COUTURIER *et al.*, APPS, and KUYUNKO *et al.*). This selected value was combined with the selected $\Delta G^{\circ}_{f,298}[Al^{3+}(aq)]$ that leads directly to the listed $\bar{S}^{\circ}_{298}[Al^{3+}(aq)]$. This latter value is consistent with the values listed or calculated by COUTURIER *et al.*, WAGMAN *et al.*, and KUYUNKO *et al.* (1983), but not with those listed by HEMINGWAY and ROBIE or APPS, mostly because of the differences in the selected $\Delta G^{\circ}_{f,298}[Al^{3+}(aq)]$.

The $\Delta G^{\circ}_{f,298}$, $\Delta H^{\circ}_{f,298}$, and $\bar{S}^{\circ}_{298}$ values for $[AlOH^{2+}(aq)]$ were selected from COUTURIER *et al.* The choice of $\Delta G^{\circ}_{f,298}[AlOH^{2+}(aq)]$ is within expected uncertainties of other selections (WAGMAN *et al.*, BERSILLON *et al.*) but different by more than expected amounts for others (HEM, MAY *et al.*, 1984; HEMINGWAY). Our selected value for $\Delta H^{\circ}_{f,298}[AlOH^{2+}(aq)]$ is in reasonable agreement with that from KUYUNKO *et al.*

There is a distinct lack of reliable experimental data to allow unambiguous critical selections for the higher hydrolyzed species (except aluminate ion as discussed later). The selected $\Delta G^{\circ}_{f,298}[AlOH^{+}_{2}(aq)]$ was taken from HEM, as calculated from the data of RAUPACH (1963). This chosen value is within expected uncertainties of other selections (HEMINGWAY, HEMINGWAY and ROBIE, BERSILLON and MAY *et al.*). The $\Delta G^{\circ}_{f,298}[AlOH^{\circ}_{3}(aq)]$ was taken from TREMAINE (1988), in disagreement with the selection from BERSILLON *et al.*

The $\Delta G^{\circ}_{f,298}$, $\Delta H^{\circ}_{f,298}$, and $\bar{S}^{\circ}_{298}$ for $[Al(OH)^{-}_{4}(aq)]$ were taken from the results listed in Chapter 7. The $\Delta G^{\circ}_{f,298}$ and $\bar{S}^{\circ}_{298}$ values are in agreement with those calculated by COUTURIER *et al.*, and the selected $\Delta H^{\circ}_{f,298}$ value is consistent with the choice of WAGMAN *et al.*, but inconsistent with that of MAY *et al.* and several others.

It should be noted that many of the discrepancies displayed between different works (especially results obtained in alkaline solutions) are due to uncertainties and differences in the equilibrium solid phase in solubility studies (see the detailed discussion by MAY *et al.*). The analysis of experimental data for the solubility of boehmite in Chapter 7 is not complicated by these problems associated with gibbsite solubilities. It is also clear that different choices of the thermodynamic properties at room temperature will lead to different values for many thermodynamic properties at higher temperatures.

Table 10.1: Selected and calculated thermodynamic properties at 25°C.*

Species	ΔG_f° (kJ mol^{-1})	ΔH_f° (kJ mol^{-1})	$\bar{S}^\circ$ (J K^{-1}mol^{-1})
$Al^{3+}(aq)$	−483.7	−531.4	−327.7
$AlOH^{2+}(aq)$	−692.5	−765.3	−178.6(−176.2)
$Al(OH)_2^+(aq)$	−908.3	(−1014.5)	(−57.3)
$Al(OH)_3(aq)$	−1075.4	(−1181.0)	(178.0)
$Al(OH)_4^-(aq)$	−1305.6	−1500.6	111.3

* Values in parenthesis are based on the present model as discussed in the text.

10.3.3 Results

Values of $\bar{S}^\circ - \Delta S_{Born}$ for each of the aluminum species with known thermodynamic properties (see Table 10.1) were calculated and are plotted versus the number of hydroxide ligands in Figure 10.1.

As can be seen in Figure 10.1, the entropies of species of the type $Al(OH)_n^{3-n}(aq)$ vary in linear fashion for the limited data available ($n = 0, 1, 4$). These linear changes support in principle the crude model proposed. As mentioned earlier, it is believed that differences in the thermodynamic properties of ions with increasing numbers of hydroxide ligands are the sum of "structural" and electrostatic contributions, and that changes in coordinated water can account for the observed "structural" differences.

It is possible to treat the end members of the hydrolysis scheme [i.e. $Al^{3+}(aq)$ and $Al(OH)_4^-(aq)$] as being the *only* known properties (as is true for volumes and heat capacities) and compare interpolated values with those known from experimental data. These calculations have been done, results of which are listed as italicized values in Table 10.1. The only case for comparison is in the value of $\bar{S}^\circ_{298}$ for $Al(OH)^{2+}(aq)$. It can be seen that the result from the calculation is in excellent agreement with the previously selected value, well within expected uncertainties (greater than 15 J $K^{-1}mol^{-1}$). The plotted line in Figure 10.1 joins values for the two end members in the hydrolysis sequence, where it can be seen that the entropy (on this scale) of $Al(OH)^{2+}(aq)$ agrees exactly with the prediction.

The difference in thermodynamic properties of $M(OH)_4^-(aq)$ and $M(OH)_3(aq)$ is assumed to be represented by the difference in the same properties for $B(OH)_4^-(aq)$ and $B(OH)_3(aq)$, which in turn can be related to the residual "structural" term due to coordinated water molecules on the solute. The entropy difference between $Al(OH)_4^-(aq)$ and $Al(OH)_3(aq)$ can therefore be predicted from data for the solutes $B(OH)_4^-(aq)$ and $B(OH)_3$ from values listed in the NBS tables (WAGMAN *et al.*, 1982). This calculation leads to $\bar{S}^\circ[Al(OH)_3] = 171$ J $K^{-1}mol^{-1}$, which is in reasonable agreement with the value 178.0 J $K^{-1}mol^{-1}$ that can calculated by assuming that the neutral solute in the hydrolysis sequence differs from the model-predicted value by the thermodynamic properties associated with two molecules of water (i.e.

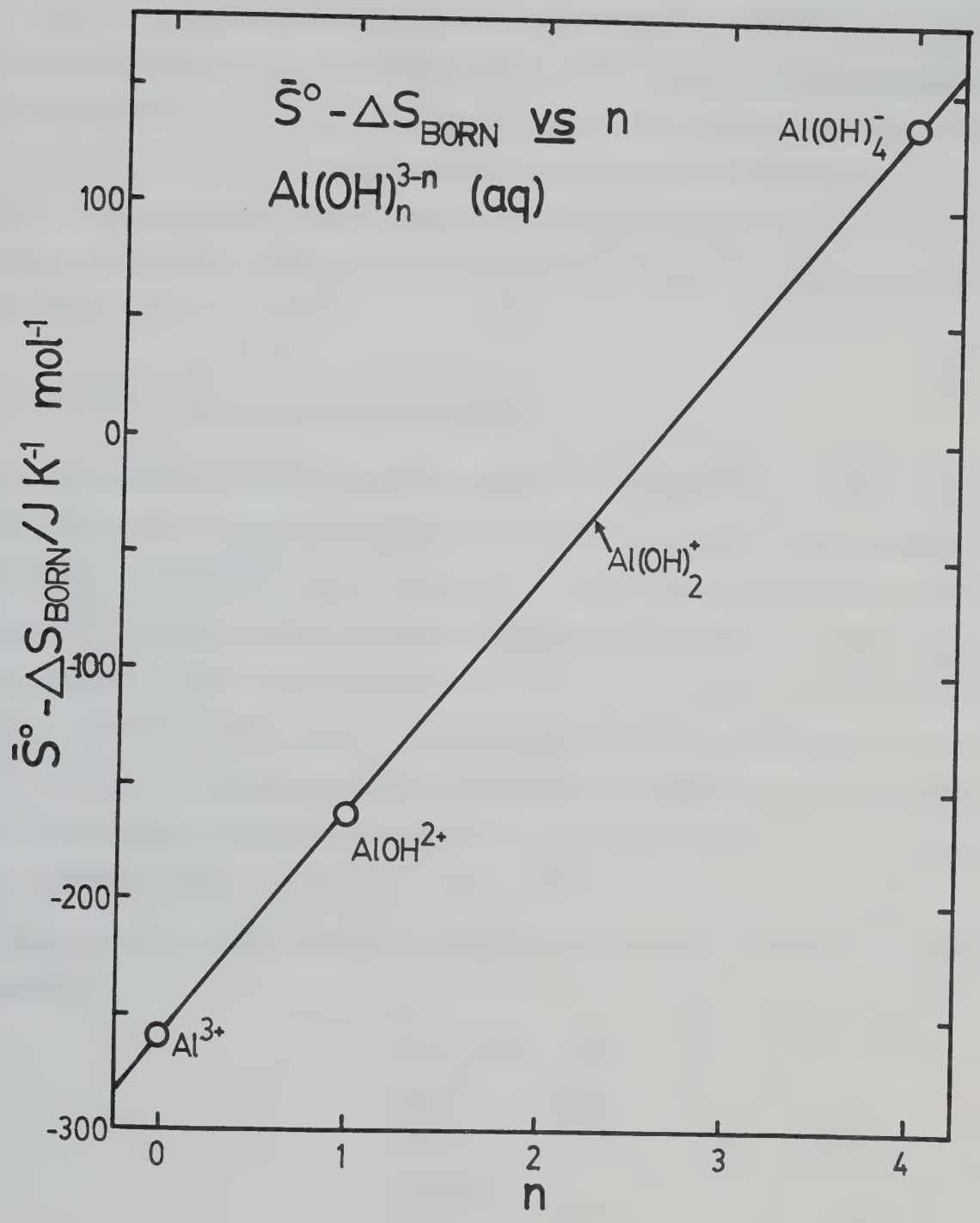

Figure 10.1: Plot of conventional ionic entropies of aqueous aluminum species minus electrostatic contributions against number of hydroxide ligands.

the neutral species has two water molecules less associated with it compared to the normal trend if it were an ionic solute). This crude assumption represents a first approximation that can be tested later by comparison with experimental results. It is assumed that the thermodynamic properties associated with two water molecules can be used over the temperature range 10 to 55°C to calculate the properties of the neutral solute from "expected" values based on plots of the conventional properties minus the appropriate Born terms as shown in Figure 10.1. A summary of all of the selected thermodynamic properties and calculated values from the present scheme is given in Table 10.1. Thermodynamic values for water were taken from the NBS tables (WAGMAN *et al.*, 1982).

10.3.4 Heat Capacities and Volumes

The basic method described above can now be extended to standard state partial molar volumes and heat capacities for Al^{3+} and $Al(OH)_4^-(aq)$ (Chapter 7) and $B(OH)_3(aq)$ and $B(OH)_4^-(aq)$ (Chapter 8). Equations 10.5 and 10.6 showed the "electrostatic" contributions to heat capacities and volumes as estimated by the Born equation. The conventional ionic properties $\bar{C}_p^\circ$ and $\bar{V}^\circ$ were calculated for each of the intermediate species in the aluminum hydrolysis scheme at 10, 25, 40, and 55 °C where the experimental data for Al^{3+} and $Al(OH)_4^-(aq)$ are available. The conventional standard state values for Al^{3+} and $Al(OH)_4^-(aq)$ and the calculated values for the intermediate species are given in Table 10.2.

Heat capacities and volumes are related to equilibrium constants (and Gibbs free energies) by

$$\Delta G^\circ = -RT \ln K \tag{10.8}$$

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \tag{10.9}$$

$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_p = \Delta \bar{C}_p^\circ \tag{10.10}$$

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta \bar{V}^\circ}{RT} \tag{10.11}$$

Heat capacities and volumes can be used to calculate equilibrium constants and other thermodynamic properties at elevated temperatures and pressures over a range in

Table 10.2: Conventional ionic properties for aluminum and hydrolyzed aluminum ions from 10 to 55°C.

Ion(aq)	t (°C)	$\bar{V}^\circ$ ($cm^3 mol^{-1}$)	$\bar{C}_p^\circ$ ($J\ K^{-1} mol^{-1}$)
Al^{3+}	10	−43.2	−138.4
	25	−44.7	−119.3
	40	−46.0	−110.5
	55	−47.3	−108.2
$AlOH^{2+}$	10	−17.5	−26.5
	25	−17.7	−24.0
	40	−18.0	−19.2
	55	−18.4	−29.4
$Al(OH)_2^+$	10	5.0	36.7
	25	6.0	71.2
	40	6.3	92.4
	55	6.4	105.9
$Al(OH)_3$	10	61.4	215.6
	25	63.3	252.6
	40	64.0	275.6
	55	64.8	289.1
$Al(OH)_4^-$	10	43.6	59.1
	25	46.3	96.5
	40	47.0	119.1
	55	47.3	129.0

which these data are known so long as some room temperature and low pressure data are known (see Chapter 7). The integrated version of these three equations that relate the Gibbs free energy to heat capacities, volumes, and room temperature properties is the familiar equation shown below:

$$\Delta G^\circ_{T,p} = \Delta G^\circ_{f,298} - \bar{S}^\circ_{298}(T - 298.15) + \int_{298}^{T} \bar{C}^\circ_p dT - T\int_{298}^{T} \frac{\bar{C}^\circ_p}{T} dT + \int_1^p \bar{V}^\circ dp \quad (10.12)$$

It is apparent that if the model is extended to predict the thermodynamic properties for the intermediate species at elevated temperatures, then various high temperature equilibria involving these species could also be calculated.

The results that have been obtained by the present scheme can be combined with the Helgeson-Kirkham-Flowers (HKF) model (HELGESON and KIRKHAM, 1974a,b, 1976 ; HELGESON *et al.*, 1981) as discussed in the preceding three Chapters. The temperature dependences of standard state volumes and heat capacities are described in terms of the HKF model by

$$\bar{V}^\circ = \sigma + \frac{\xi T}{T - \theta} + \Delta V_{Born} \quad (10.13)$$

and

$$\bar{C}^\circ_p = c_1 + \frac{c_2 T}{T - \theta} + \Delta C_{p,Born} \quad (10.14)$$

where the first two terms in each equation precisely fit the low temperature data and are used to define the fitting coefficients σ, ξ, c_1, c_2, and θ. The contributions from the Born equation are used to guide extrapolations to higher temperatures. Application of these equations to the results that are listed in Table 10.2 are summarized in Table 10.3. Indicative results for the species of aluminum are shown in Figure 10.2 by plots of the temperature dependence of the standard state heat capacities for all of the desired species.

It was found that fitting equations of type 10.13 and 10.14 to the results in Table 10.2 generated slightly different θ values for heat capacities and volumes. Because of the larger contribution that the integrated heat capacity function makes at elevated temperatures to the Gibbs free energies, the volumetric data were fitted again using values of θ evaluated from the fits to the heat capacity data. All of the appropriate quantities including radii that are required in the calculations described above are given in Table 10.3.

Table 10.3: Parameters from HKF model for selected species of aluminum.

Species	σ	ξ	$10^{-5}\omega*$	θ	c_1	c_2
	(cm^3mol^{-1})		(K)	$(J\ mol^{-1})$	$J\ K^{-1}mol^{-1})$	
$Al^{3+}(aq)$	−41.58	0.8331	11.84	235.2	103.73	−23.567
$AlOH^{2+}(aq)$	−16.67	0.1112	2.801	238.1	145.67	−23.525
$Al(OH)_2^+(aq)$	7.80	−0.4592	−0.617	239.4	190.24	−24.579
$Al(OH)_3(aq)$	69.18	−1.1598	0	239.8	386.91	−26.240
$Al(OH)_4^-(aq)$	56.20	−1.4490	4.461	241.9	278.22	−26.289

* ω values were evaluated using ionic radii from SHANNON (1976) and parameters to convert them to "effective" aqueous radii from HELGESON *et al.* (1981) as discussed in the text. The effective aqueous radii used were 3.36, 3.80, 4.24, 3.05, and 3.15 Å from $Al^{3+}(aq)$ to $Al(OH)_4^-(aq)$, respectively.

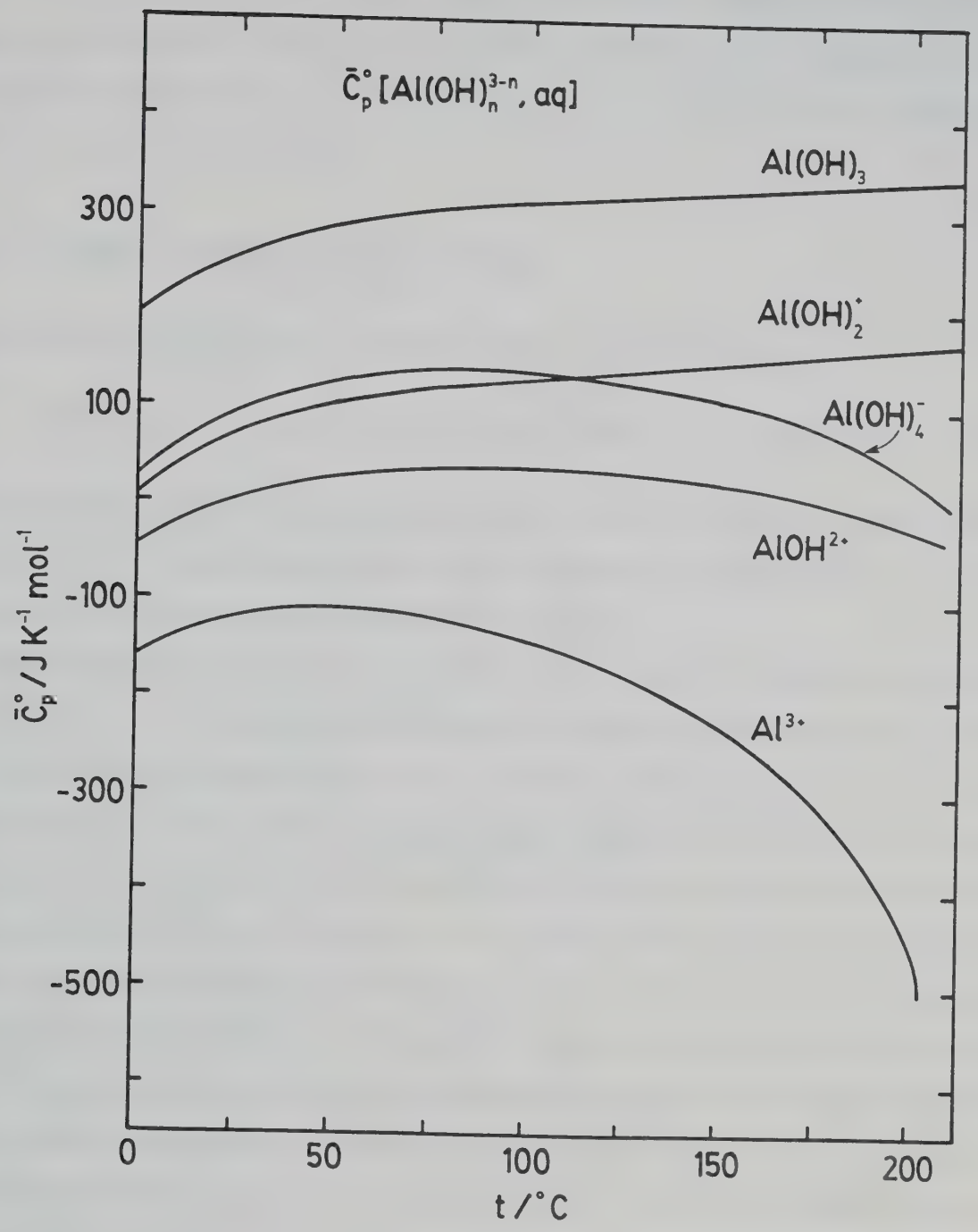

Figure 10.2: Heat capacities of aqueous aluminum ion and its mononuclear hydrolyzed species.

Now that expressions that predict the high temperature heat capacities and volumes have been derived, expressions for most of the species can be tested in terms of experimental results. The best such test is provided by mineral solubility data over ranges of pH values so that reactions involving all of the species are important. One of the best known sets of mineral solubilities as a function of pH and temperature is that for boehmite [AlOOH(c)].

10.4 Test: Boehmite solubility

The solubility of the mineral boehmite can be represented by

$$\mathrm{AlOOH(c) + (3 - n)H^+(aq) = Al(OH)_n^{3-n}(aq) + (2 - n)H_2O(l)} \qquad (10.15)$$

Experimental solubility results are available to 250°C (KUYUNKO *et al.*, 1983). The most severe test using these data is at the highest temperature where errors associated with the present approach should be largest.

High temperature Gibbs free energies were calculated using the selected room temperature values that are listed in Table 10.1 along with thermodynamic properties for boehmite from HEMINGWAY *et al.* (1978), values for water from HELGESON and KIRKHAM (1974), and the present heat capacity and volume expressions for the aqueous and hydrolyzed metal species. Calculations were performed using the computer code SUPCRT (KIRKHAM *et al.*, 1978). The resulting high temperature Gibbs energies for reactions with various n were used to calculate the speciation as a function of temperature and pH at 250°C. The equilibrium speciation calculations were based on exposure of a solution of known pH at 25°C to the appropriate mineral at the higher temperature of interest (see detailed discussion by TREMAINE *et al.*, 1977) by an iterative calculation procedure using a simple two parameter extended Debye-Hückel equation for activity coefficients. For comparison with experimental results, these calculations referenced to 25°C will be used rather than the calculated high temperature equilibrium pH.

The results of these calculations are shown in graphical form in Figure 10.3. It can be seen that there is no significant difference between the present calculated values and the experimental results of KUYUNKO *et al.* (1983). A previous analysis

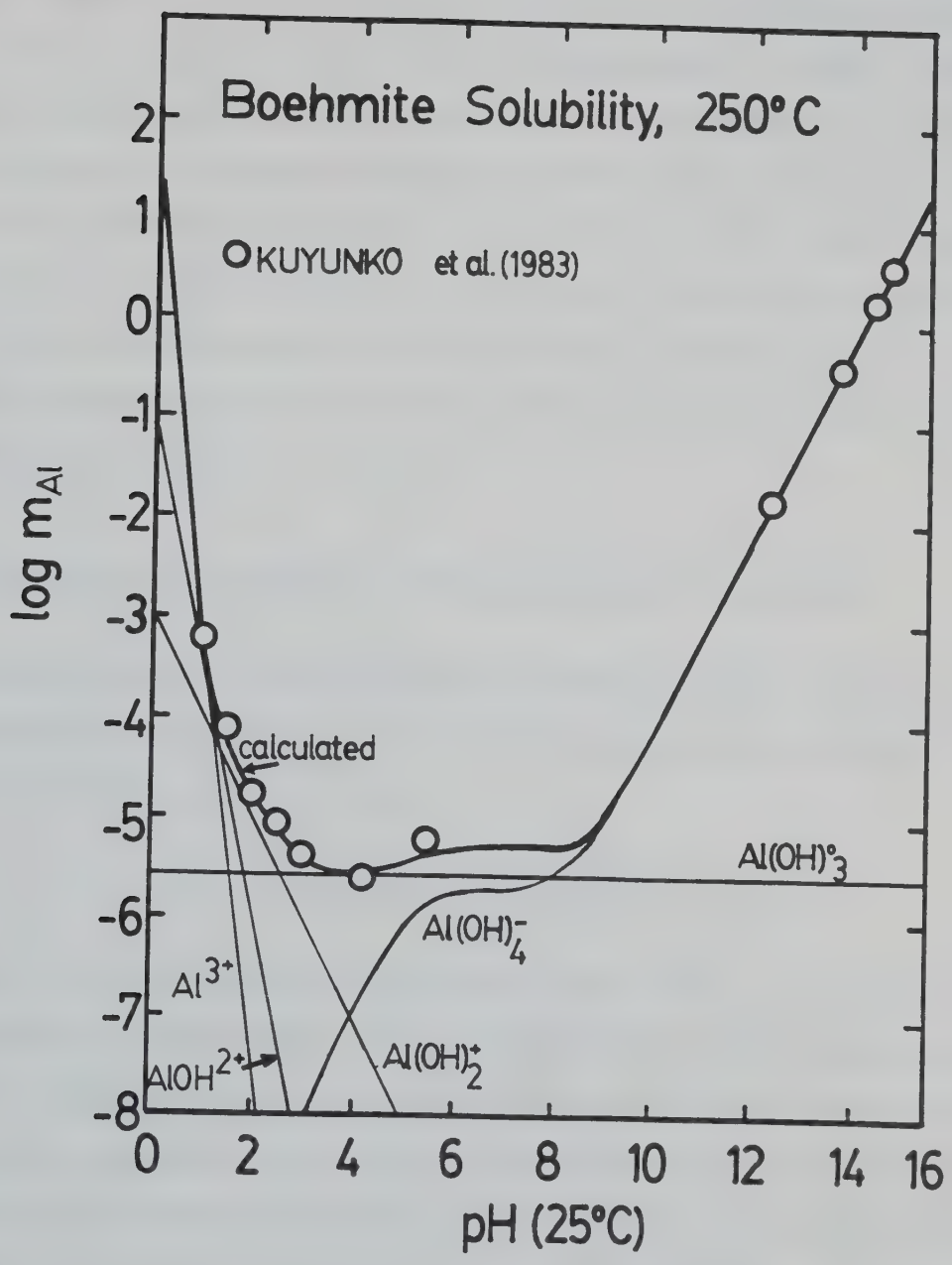

Figure 10.3: Comparison of experimental solubilities for boehmite with those calculated by the present scheme. Contributions to the total solubility from each species present are shown in the figure. The sum of these contributions is indicated by the thick line.

(TREMAINE, 1988) of this same system using a different approach with the same auxiliary data for the species reported in Chapters 6 and 7 shows less good agreement, especially in the pH regions where contributions from the neutral solute become important. Since the contributions of $Al^{3+}(aq)$ and $Al(OH)_4^-(aq)$ are by far the largest at low and high pH values, only the intermediate region provides a real test of the present methods and calculations. It is apparent that consideration of only the monomeric hydrolysis products [neglect of the several known polymeric species, see for example MACDONALD and BUTLER (1972), MACDONALD *et al.* (1973), BAES and MESMER (1976), and MESMER *et al.* (1971)] provides excellent agreement with the experimental results at 250°C. It is also apparent that several of the "first approximations" used in the development of the present approach are entirely adequate to 250°C.

10.5 General equations and extension of model

It is appropriate now to list the equations that should be used to calculate properties of the intermediate mononuclear species in the aluminum-water system. From 10 to 55°C these equations are of the form

$$(\bar{Y}^\circ - \bar{Y}_{Born})[Al(OH)_n^{3-n},\ aq] = a_Y + b_Y n \qquad (10.16)$$

where a and b are the intercept and slope of plots of the type shown for the conventional ionic entropies of these species in Figure 10.1. These equations are useful for all ionic species, and the properties for the neutral species can be calculated from the value calculated by eq. 10.16 in combination with the properties for pure water at the temperature of concern as discussed earlier. The values of the a and b parameters for entropies, volumes and heat capacities are given in Table 10.4.

Since these equations were defined specifically for the aluminum water system, it is appropriate to check their applicability to other systems. Because of the excellent agreement of calculated and experimental solubilities for boehmite, a more detailed theoretical consideration of the changes accompanying hydrolysis was not warranted.

Table 10.4: Parameters in equations of type 10.16 for predicting properties of intermediate mononuclear species in the aluminum-water system for $Al(OH)_n^{3-n}(aq)$.

t (°C)	a_S (J $K^{-1}mol^{-1}$)	b_S	a_V (cm^3mol^{-1})	b_V	a_C (J $K^{-1}mol^{-1}$)	b_C
10			−36.6	20.65	−35.5	33.35
25	−259.0	99.1	−37.7	21.63	−7.7	36.55
40			−38.2	21.98	8.5	38.85
55			−38.6	22.28	20.8	39.20

10.6 Extension to the iron-water system

The results described in the preceding section showed that low temperature heat capacity and volume values can be used for the calculation of high temperature solubilities of aluminum-containing minerals. It is of interest to test if these results can be extended to the calculation of solubilities of iron-containing minerals. An important iron-containing mineral is magnetite (Fe_3O_4), which contains both iron(II) and iron(III) ions. Another iron mineral is hematite (Fe_2O_3), which contains iron only in the 3+ oxidation state. Because the previous equations were developed specifically for the hydrolysis of $Al^{3+}(aq)$, it is thought that these equations will be useful in describing the Gibbs free energies for species involved in the hydrolysis of iron(III) since the available evidence suggests that the mononuclear hydrolysis products are iso-structural with those in the aluminum system BAES and MESMER, 1976). There are recent data available for the solubility of hematite to 200°C (SERGEYEVA *et al.*, 1988) and comprehensive data for the solubility of magnetite as functions of temperature, pH, and hydrogen gas concentration to 300°C (SWEETON and BAES, 1970; TREMAINE and LEBLANC, 1980).

10.6.1 Selection of thermodynamic properties at 25°C

Some thermodynamic properties for iron(II) and iron(III) were selected in the preceding Chapter. None of these selections, however, included values for the hydrolyzed species. For a discussion of the selected room temperature thermodynamic properties for iron(II) and iron(III), the reader is directed to Chapter 9.

Selected values for all iron species of present interest are listed in Table 10.5. The choices for these values come from the sources cited below. For the hydrolyzed ferric species, the works of MESMER and BAES (1976), and TREMAINE and LEBLANC (1980) have reviewed most ealier pertinent works and have recommended "best" values based mostly on their own results. Reasonably reliable values for the thermodynamic properties of hydrolyzed species are also available from the NBS tables (WAGMAN *et al.*, 1982), all referenced to their selections for the properties of ferric ion. We have selected the value for $\Delta G^\circ_{f,298}[Fe(OH)^{2+}(aq)]$ based on the cited NBS value adjusted to allow for our selection of $\Delta G^\circ_{f,298}[Fe^{3+}(aq)]$. Similar calculations

lead to the selected value for $\Delta G^{\circ}_{f,298}[Fe(OH)^{+}_{2}(aq)]$. Thermodynamic properties for neutral solutes determined from sparingly soluble metal hydroxides are among the most difficult to evaluate. The selections of BAES and MESMER (1976) indicate a $\Delta G^{\circ}_{f,298}[Fe(OH)_3(aq)] >$ -658 kJ mol^{-1} and those of TREMAINE and LEBLANC (1980) > -660 kJ mol^{-1}. Interpolation of the better known $\Delta G^{\circ}_{f,298}$ values for the first two hydrolyzed species and $Fe(OH)^{-}_{4}(aq)$ lead to the reported $\Delta G^{\circ}_{f,298}[Fe(OH)_3(aq)]$ listed in Table 10.5. It appears from subsequent calculations that even this value is too negative and also too uncertain to be meaningful and thus was ignored in further calculations. The $\Delta G^{\circ}_{f,298}[Fe(OH)^{-}_{4}(aq)]$ selected by TREMAINE and LEBLANC was also used here.

All standard state entropies of the ferric species were calculated from the present scheme using the b_S constant for eq. 10.15 listed in Table 10.4 and the a_S parameter calculated from the cited standard state entropy of $Fe^{3+}(aq)$ listed in Table 10.5. All enthalpy values were calculated from the listed Gibbs free energies and corresponding standard state entropies. It should be noted that all of these selections for the ferric ion species are important for calculations of the solubility of hematite yet less important for calculations of the solubility of magnetite. Because of the greater stability of ferrous ion species in the magnetite system, only these quantities need be known accurately for a description of high temperature solubilities.[1]

Selections for the ferrous ion species are also listed in Table 10.5. Sources cited above and the works by TREMAINE *et al.* (1977) and SWEETON and BAES (1970) are useful for evaluation of much of the available thermodynamic quantities at room temperature. The listed $\Delta G^{\circ}_{f,298}[FeOH^{+}(aq)]$ value was calculated from MESMER (1971) and the cited value for $\Delta G^{\circ}_{f,298}[Fe^{2+}(aq)]$. The value $\Delta H^{\circ}_{f,298}[FeOH^{+}(aq)]$ from BOLZAN and ARVIA (1963) was used to calculate $\bar{S}^{\circ}_{f,298}[FeOH^{+}(aq)]$ along with the selected value for the Gibbs free energy. All thermodynamic properties for both $Fe(OH)_2(aq)$ and $Fe(OH)^{-}_{3}(aq)$ were taken from TREMAINE and LEBLANC (1980).

[1] SWEETON and BAES (1970) could fit their results quite accurately using values for only these species.

Table 10.5: Selected and calculated thermodynamic properties at 25°C.

Species	ΔG_f° (kJ mol^{-1})	ΔH_f° (kJ mol^{-1})	$\bar{S}^\circ$ (J K^{-1}mol^{-1})
$Fe^{3+}(aq)$	−15.0	−47.7	−278.4
$FeOH^{2+}(aq)$	−239.7	(−297.5)	(−129.2)
$Fe(OH)_2^+(aq)$	−448.3	(−540.4)	(−11.2)
$Fe(OH)_3(aq)$	(−633.9)	(−725.5)	(223.9)
$Fe(OH)_4^-(aq)$	−840.2	(−1021.1)	157.6(156)
$Fe^{2+}(aq)$	−89.3	−90.4	−107.1
$FeOH^+(aq)$	−272.3	−326.1	−50.5
$Fe(OH)_2(aq)$	−441.0	−540.6	29.1
$Fe(OH)_3^-(aq)$	−605.1	−774.0	29.9

Values in parentheses represent estimates and calculations using the present model. Selections of all of these values are discussed in the text.

10.6.2 Test: Hematite solubility at 200°C

The solubility of hematite in aqueous solution can be represented by

$$Fe_2O_3(c) + (6 - 2n)H^+(aq) = 2Fe(OH)_n^{3-n}(aq) + (3 - 2n)H_2O(l) \qquad (10.17)$$

Some solubility results have recently become available at 200°C (SERGEYEVA *et al.*, 1988) for $n = 0$ and $n = 4$. These results can be summarized by $\log K = -7.10 \pm 0.6$ for the reaction represented by eq. 10.17 with $n = 0$ and $\log K = -9.12 \pm 0.2$ for the reaction represented by eq. 10.17 with $n = 4$ at 200°C.

The present calculations employ the b_Y coefficients listed in Table 10.4 in combination with a_Y parameters defined by one of the species in the present system. The results of Chapter 9 that provided standard state partial molar volumes and heat capacities for $Fe^{3+}(aq)$ will be used to generate these a_Y terms. Calculations identical to those described previously have lead to the conventional ionic volumes and heat capacities for all of the aqueous ferric species that are listed in Table 10.6. These values were used in HKF fits of the type described earlier, results of which are reported in Table 10.7. Plots of the temperature dependence of the heat capacities for all of these species are shown in Figure 10.4.

Calculations similar to those described for the solubility of boehmite were carried out for the solubility of hematite. The parameters in Table 10.7 were used in the computer code SUPCRT to generate Gibbs free energies to 300°C. These free energies were used to calculate concentrations of species present in an aqueous solution in equilibrium with hematite. The results of all of these calculations are shown in Figure 10.5 along with experimental results from SERGEYEVA *et al.* (1988) [using auxiliary data for the dissociation constant of water at 200°C from BUSEY and MESMER (1978)]. The present scheme provides estimations of the contributions of all species to the total solubility of hematite. These predictions are well within experimental errors for $FeOH^{2+}(aq)$ and are in very good agreement with the contribution of $Fe(OH)_4^-(aq)$ as can be seen in the Figure. The selected value of the Gibbs free energy of $Fe(OH)_4^-(aq)$ at 25°C differs from that selected by SERGEYEVA *et al.* (1988) by 5.2 kJ mol^{-1}. If the value selected by SERGEYEVA *et al.* were used in the present calculations, the difference in the log of the concentration of $Fe(OH)_4^-(aq)$ would decrease to 0.05. This result is in excellent agreement with the experimental

Table 10.6: Conventional ionic properties for ferric ion and its corresponding mononuclear hydrolyzed ions from 10 to 55°C.

Ion(aq)	t (°C)	$\bar{V}^\circ$ ($cm^3 mol^{-1}$)	$\bar{C}_p^\circ$ ($J\ K^{-1} mol^{-1}$)
Fe^{3+}	10	−36.4	−151.1
	25	−33.8	−105.2
	40	−36.9	−86.2
	55	−42.7	−57.1
$FeOH^{2+}$	10	−11.0	−42.6
	25	−7.0	12.9
	40	−9.2	39.7
	55	−14.0	76.4
$Fe(OH)_2^+$	10	11.6	19.1
	25	16.6	80.1
	40	14.9	111.2
	55	10.7	151.1
$Fe(OH)_3$	10	67.9	197.8
	25	73.9	261.1
	40	72.7	294.0
	55	69.0	333.8
$Fe(OH)_4^-$	10	50.0	41.9
	25	56.8	105.6
	40	55.5	138.1
	55	51.5	174.4

Table 10.7: Parameters from HKF model for selected species of aluminum.

Species	σ	ξ	$10^{-5}\omega*$	θ	c_1	c_2
	(cm^3mol^{-1})		(K)	(J mol^{-1})	J $K^{-1}mol^{-1}$)	
$Fe^{3+}(aq)$	−44.25	4.8855	11.25	201.6	399.6	−129.93
$FeOH^{2+}(aq)$	−15.77	2.3908	2.596	208.7	414.7	−113.97
$Fe(OH)_2^+(aq)$	11.02	0.7784	−0.659	212.8	445.7	−107.12
$Fe(OH)_3(aq)$	74.64	−0.9058	0	215.1	635.8	−105.0
$Fe(OH)_4^-(aq)$	62.82	−1.6081	4.393	219.8	510.9	−96.187

* ω values were calculated using ionic radii from SHANNON (1976) and parameters from HELGESON *et al.* (1981) to convert them to "effective" aqueous radii as discussed in the text. The effective aqueous radii were 3.47, 3.91, 4.35, 3.17, and 3.25 Å from $Fe^{3+}(aq)$ to $Fe(OH)_4^-(aq)$, respectively.

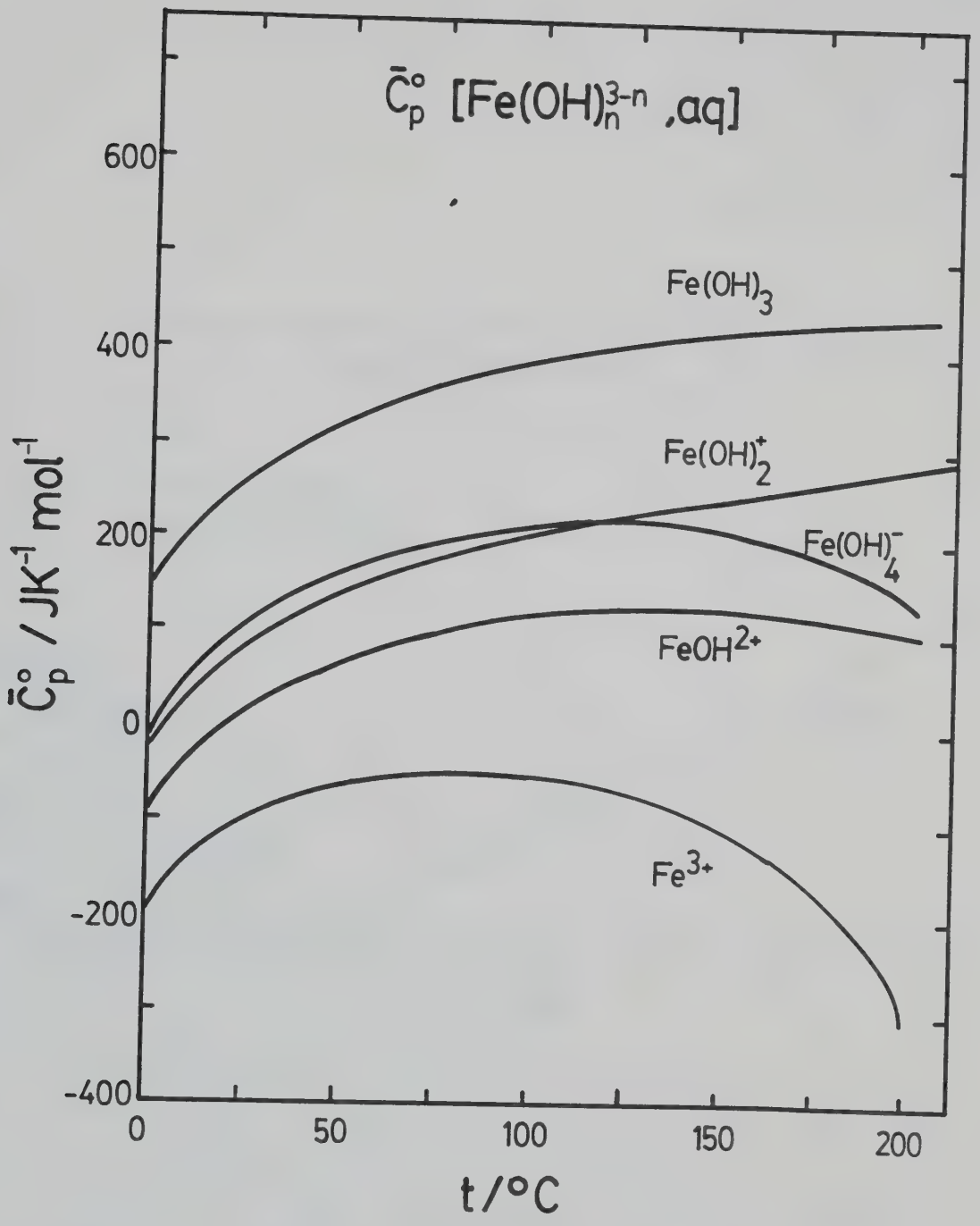

Figure 10.4: Heat capacities of aqueous ferric ion and its mononuclear hydrolyzed species.

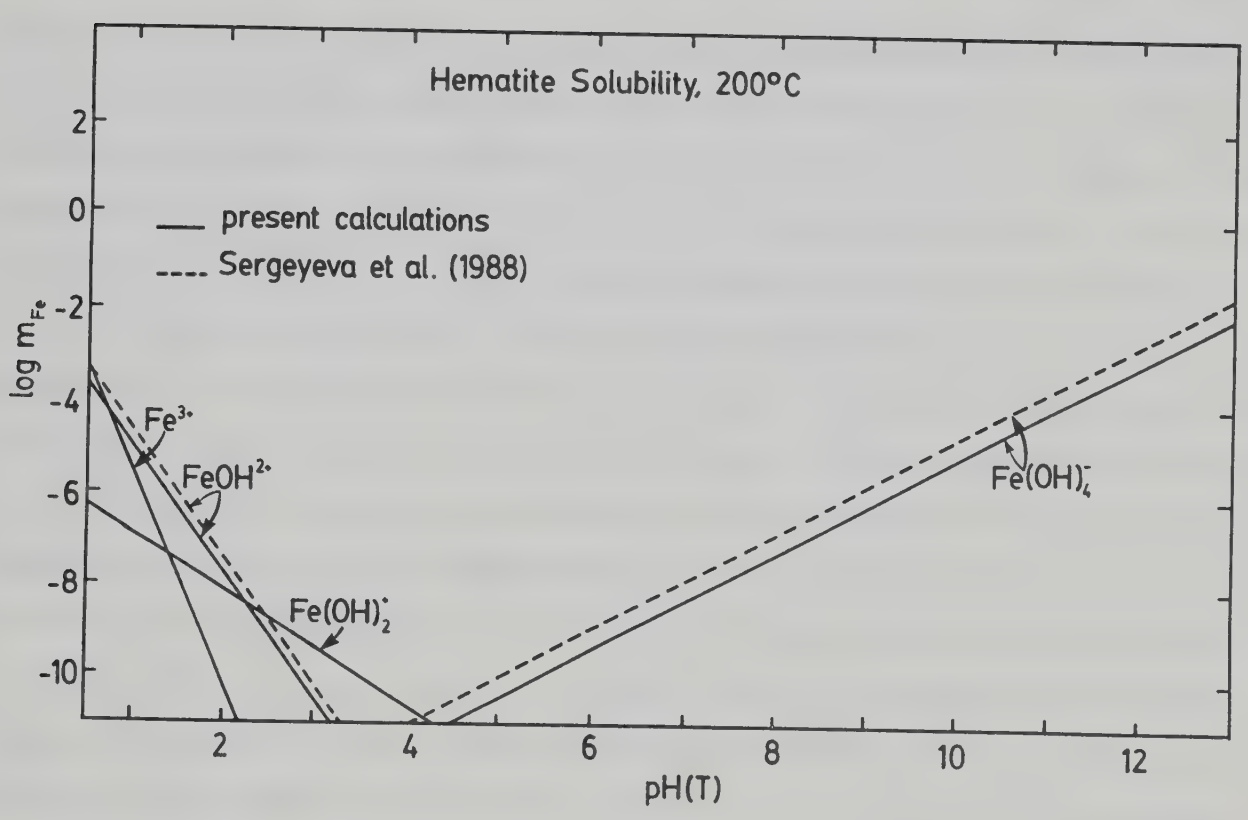

Figure 10.5: Comparison of experimental stabilities for aqueous ions from the solubility of hematite with those calculated by the present scheme. The dotted lines are calculations based on the limited data SERGEYEVA *et al.* (1988) from results of solubilities in acidic and alkaline solutions. The solid lines are calculations based on the present scheme for all mononuclear ions in the ferric-water system.

results. This example clearly shows the power of this simple scheme for these types of calculations to 200°C so long as the heat capacities of the unhydrolyzed 3+ metal cation are known.

10.6.3 Test: Magnetite solubility

The solubility of magnetite can be represented by the following two equations:

$$Fe_3O_4(c) + (6 - 3n)H^+(aq) + H_2(g) = 3Fe(OH)_n^{2-n}(aq) + (4 - 3n)H_2O(l) \quad (10.18)$$

$$Fe_3O_4(c) + (9 - 3n)H^+(aq) = 3Fe(OH)_n^{3-n}(aq) + \frac{1}{2}H_2(g) + (4 - 3n)H_2O(l) \quad (10.19)$$

The first equation shows the contribution to the total solubility from ferrous species and the second from ferric species. Since the model summarized here was developed specifically using data for the hydrolysis of a 3+ cation, successful extension of the present scheme to include the hydrolysis of 2+ ions seems doubtful. As can be calculated from the data in Table 10.5, the equations developed for the entropies of the hydrolysis products of 3+ cations do not adequately represent these same properties for the hydrolysis of $Fe^{2+}(aq)$. In all cases this scheme overestimates the standard state entropies, thus making the calculated $\Delta H^\circ_{f,298}$ values more positive than those presently available in the literature. Of considerable uncertainty are the properties associated with the neutral solute $Fe(OH)_2(aq)$, since this species is not iso-structural with the trigonal neutral solutes of ferric and aluminum hydroxide.

Plots of $(\bar{S}^\circ - \Delta S_{Born})$ against the number of hydroxide ligands (n) for the hydrolysis reactions of 2+ ions compared with plots of these same quantities for the hydrolysis of 3+ metal ions showed that the slope of the former plots were approximately one half of those for the latter. It is likely that errors will be associated with overestimation of heat capacities and volumes for these species. Application of equations of the type represented by eq. 10.16 to the heat capacity and volume results for ferrous ion reported in Chapter 9, have resulted in the volume and heat capacities listed in Table 10.8. The heat capacity and volume values listed in Table 10.8 were used for the fitting of equations from the HKF model as described earlier. Results of these fits are reported in Table 10.9. The temperature dependence of the heat capacities of all of the appropriate ferrous species are shown in Figure 10.6 calculated from these fits.

Table 10.8: Conventional ionic properties for ferrous ion and its corresponding mononuclear hydrolyzed ions from 10 to 55°C.

Ion(aq)	t (°C)	$\bar{V}^\circ$ ($cm^3 mol^{-1}$)	$\bar{C}_p^\circ$ ($J\ K^{-1} mol^{-1}$)
Fe^{2+}	10	−22.6	−31.4
	25	−22.1	−27.3
	40	−20.9	−14.1
	55	−19.3	−9.1
$FeOH^+$	10	1.4	53.7
	25	3.1	65.3
	40	4.9	84.6
	55	7.4	95.0
$Fe(OH)_2$	10	58.1	237.9
	25	60.8	252.3
	40	63.2	273.8
	55	66.2	284.7
$Fe(OH)_3^-$	10	40.3	82.5
	25	43.7	97.3
	40	46.0	118.5
	55	48.8	125.8

Table 10.9: Parameters from HKF model for selected aqueous ferrous species.

Species	σ	ξ	$10^{-5}\omega*$	θ	c_1	c_2
	(cm^3mol^{-1})		(K)	$(J\ mol^{-1})$	$J\ K^{-1}mol^{-1})$	
$Fe^{2+}(aq)$	−12.93	−0.69711	5.935	255.3	105.17	−11.004
$FeOH^{+}(aq)$	8.815	−0.5581	−0.0146	263.8	136.96	−8.268
$Fe(OH)_2(aq)$	67.53	−0.57565	0	267.3	325.60	−7.5847
$Fe(OH)_3^-(aq)$	52.05	−0.37719	4.348	272.6	208.98	−6.0566

* ω values were calculated using ionic radii from SHANNON (1976) and parameters from HELGESON *et al.* (1981) to convert them to "effective" aqueous radii as discussed in the text. The effective aqueous radii were 2.66, 3.10, 3.24, and 3.32 Å from $Fe^{2+}(aq)$ to $Fe(OH)_3^-(aq)$, respectively.

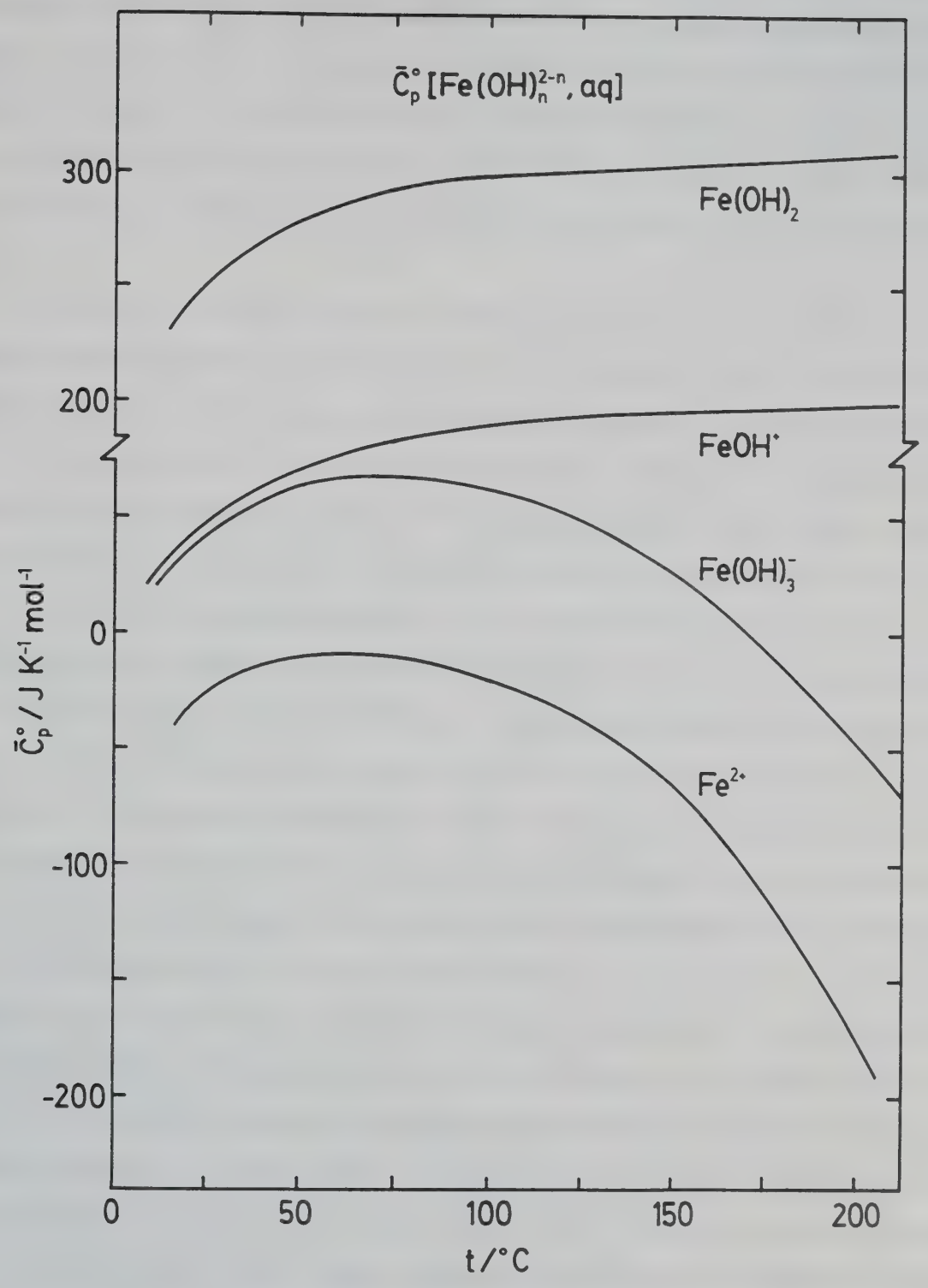

Figure 10.6: Heat capacities of aqueous ferrous ion and its mononuclear hydrolyzed species.

Speciation calculations as a function of pH and temperature were carried out as previously outlined for boehmite and hematite using high temperature Gibbs free energies for all of the reactions as calculated from the data in Table 10.8 and the computer code SUPCRT. The results of these calculations are compared with results of solubility measurements at 200°C (TREMAINE and LEBLANC, 1980) and at 300°C (TREMAINE and LEBLANC, 1980; SWEETON and BAES, 1970) in Figures 10.7 and 10.8.

The present calculations are in excellent agreement with results of direct solubility measurements from TREMAINE and LEBLANC (1980) up to pH values of approximately 9. Above these pH values, the species in the largest concentrations are $Fe(OH)_2(aq)$ and $Fe(OH)_3^-(aq)$ that we have indicated as being the least well predicted by the present approach. The good agreement at pH values below 9 suggests that the present model is applicable to the hydrolysis of 2+ ions but should be combined with experimental data for a hydrolyzed anionic species of the type $M(OH)_3^-(aq)$ for improved predictions. It should be noted that the solubility results of TREMAINE and LEBLANC (1980) are in good agreement with those from SWEETON and BAES (1970) at low values of pH, but in poor agreement for more alkaline solutions. The present calculations for 200°C are in good agreement with the results of SWEETON and BAES (1970) over the entire pH range of their measurements. The present calculations suggest that the solubility measurements from SWEETON and BAES (1970) are superior to those from TREMAINE and LEBLANC (1980) at 200°C. However, the present approach lacks the rigour necessary to make this statement completely reliable. Experimental difficulties, however, are expected to decrease the observed solubilities because of problems associated with undersaturation. As discussed at length by TREMAINE and LEBLANC (1980), their observed results that are lower than other studies are more likely correct because of various experimental difficulties that may cause higher observed solubilities. A complete unambiguous evaluation of "best" high temperature Gibbs free energies for all of the species involved will require further experimental data at temperatures over the range 25 to 300°C.

The calculated solubilities of magnetite at 300°C are shown along with direct results in Figure 10.8. These results are similiar to those at 200°C. Because of

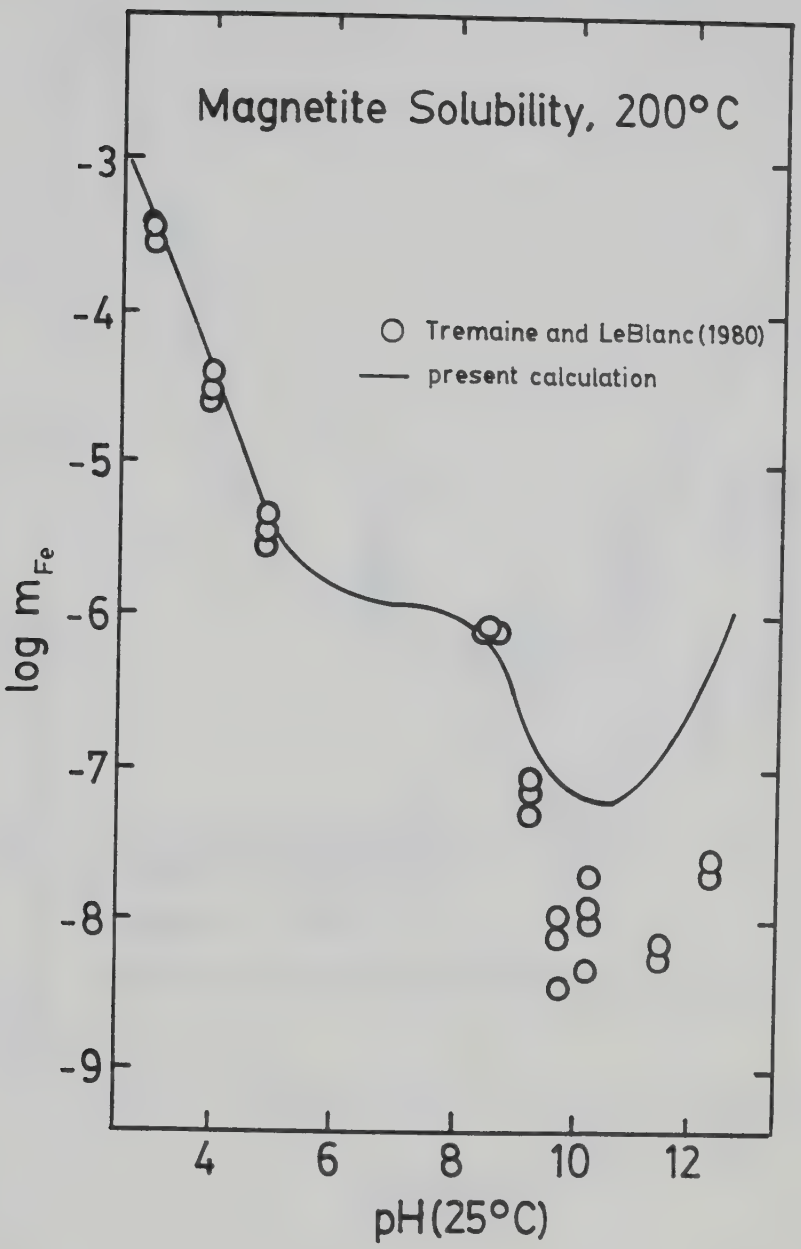

Figure 10.7: Comparison of calculated and experimental solubilities of magnetite at 200°C.

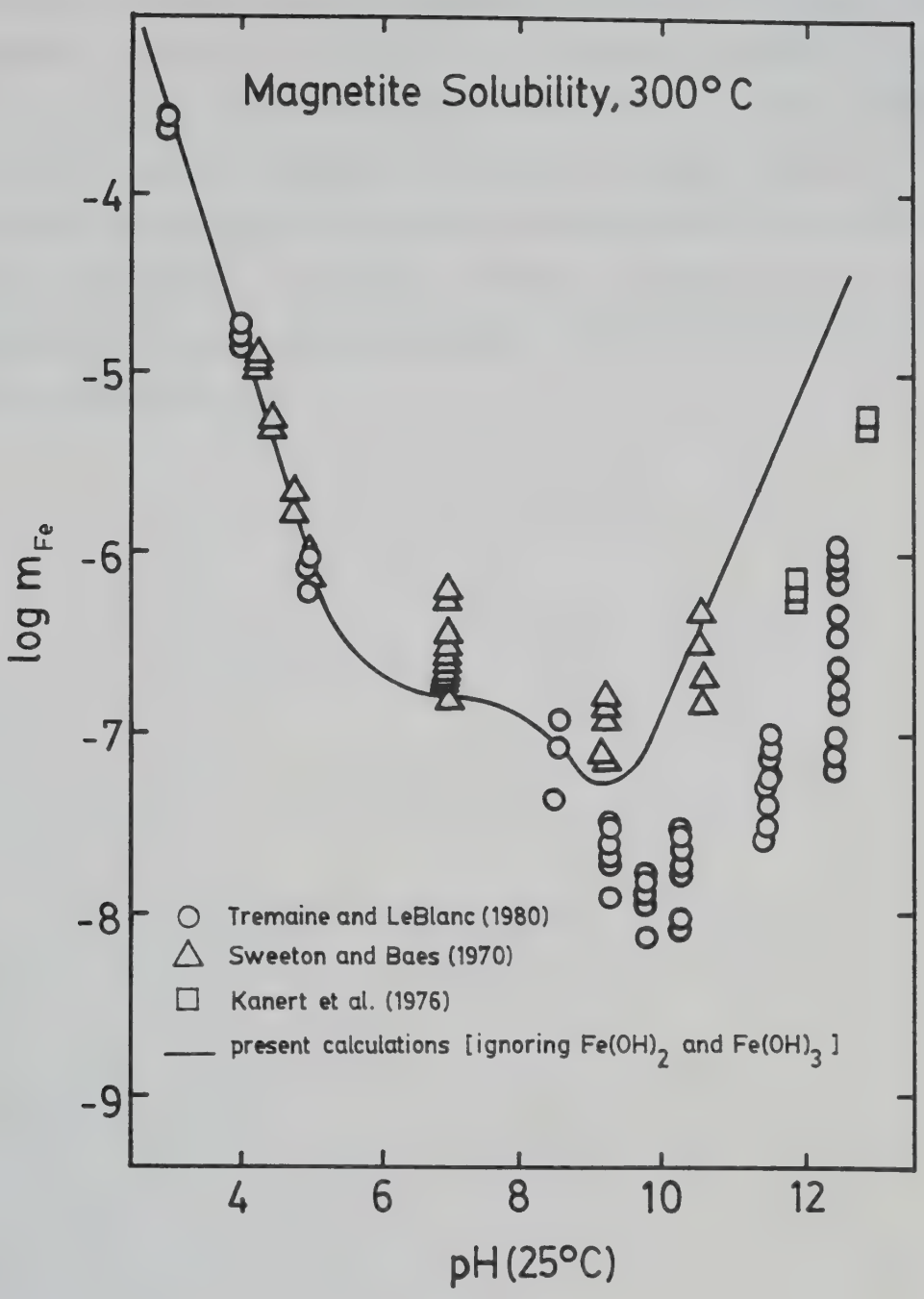

Figure 10.8: Comparison of calculated and experimental solubilities of magnetite at 300°C.

uncertainities in the thermodynamic properties of the neutral solutes at 25°C, they were not included in the present calculations [nor were they included by SWEETON and BAES (1970) in their analysis of measured solubilities]. The present calculations are in excellent agreement with all of the experimental results to a pH value of 10 and with those from SWEETON and BAES (1970) over their entire pH range. The observed differences between the presently calculated values and most of the experimental results are within the scatter amongst different works. ($\pm$ 2 in log K). The slightly more positive results from SWEETON and BAES (1970) are preferred here as being more accurate although absolute "best" value choices must be deferred until later as discussed above.

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Chapter 11

Thermodynamics of aqueous uranyl ion: Apparent and partial molar heat capacities and volumes of aqueous uranyl perchlorate from 10 to 55 °C

11.1 Introduction

Uranium and its aqueous species are fundamentally linked to numerous natural and man-made processes. In many of these applications, thermochemical data are required for calculations of speciation and various other properties for the participating uranium species. Specific examples of processes that involve aqueous uranium that require accurate thermochemical data are: calculations involving nuclear waste cycles, uranium mining, groundwater movement of radionuclides, nuclear power generation, corrosion of uranium containing systems, irradiated nuclear fuel, and the long term storage of radioactive waste. Many of these processes are associated with slightly or highly acidic environments where $UO_2^{2+}(aq)$ is the most important aqueous species of uranium.

There are many thermodynamic data available for solid state and aqueous uranium (VI) species near 25°C; more data are still required at 25°C and even more are needed for higher temperatures (LANGMUIR, 1978; LEMIRE and TREMAINE, 1980). There are apparently reliable values of the Gibbs free energy and standard state entropy of $UO_2^{2+}(aq)$ at 25°C (WAGMAN *et al.*, 1982; FUGER and OETTING, 1976). There are also a few data available for the thermodynamic properties of $UO_2^{2+}(aq)$ at high temperatures from solubility measurements. Thermodynamic data for U(VI) hydrolyzed species are less well known because of a variety of chemical and experimental problems.

Ions of the type $MO_2^{2+}(aq)$ are known to form complexes with a variety of anions such as sulphate, chloride, and nitrate. $UO_2^{2+}(aq)$ is known to form rather stable

complexes with each of these anions in aqueous solution (HÖGFELDT, 1982; SILLEN and MARTELL, 1964, 1971; SMITH and MARTELL, 1976). Many of the applications that require thermodynamic data for aqueous uranium species require data for both the uncomplexed uranyl ion as well as data for the uranyl complexes with sulphate, chloride, and nitrate. Investigations of the systems of aqueous uranyl ion with sulphate, chloride, and nitrate in terms of standard state heat capacities and volumes have been completed and are described in the following Chapter.

It is expected that minimal complexation occurs in aqueous solutions containing UO_2^{2+} when ClO_4^- is present as the anion. To date no equilibrium or spectroscopic studies (FRATIELLO *et al.*, 1970; BROOKER *et al.*, 1980) have shown any appreciable amounts of UO_2^{2+}–ClO_4^- complex at the concentrations of interest to us. Because of the relative concentrations of UO_2^{2+} and ClO_4^- in the solutions of present interest, it is believed that any complexed species that may be present have a negligible affect on the calculations that follow.

The standard state partial molar volumes and heat capacities of $UO_2(ClO_4)_2$ are desirable over wide ranges of temperature and pressure. Since these are related to the Gibbs free energy as temperature and pressure derivatives, they help to define both the high temperature and high pressure behaviour of this function. The purpose of this work is to provide expressions for the standard state heat capacity and volume of aqueous uranyl ion from 10 to 55 °C that can be used to refine several low temperature thermodynamic properties and to permit useful extrapolations of equilibrium constants or Gibbs free energies to high temperatures and pressures. Standard state volumes and heat capacities are related to equilibrium constants via the expressions

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \tag{11.1}$$

$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_p = \Delta C_p^\circ \tag{11.2}$$

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = \frac{-\Delta V^\circ}{RT} \tag{11.3}$$

Standard state heat capacities and volumes of UO_2^{2+}(aq) are also useful in testing or developing semi-theoretical models for standard state volumes and heat capacities for ions of the type MO_2^{2+}(aq).

11.2 Experimental

Water used for all experiments was first passed through an activated charcoal filter and then through a Milli-RO4/Milli-Q reagent grade mixed bed ion exchange and activated carbon system to yield purified water with a resistivity of 18 MΩ cm or greater. Solutions of NaCl (Fisher certified, ACS) were prepared by mass after drying the salt at 110 °C until constant weight.

Uranyl perchlorate hexahydrate was obtained from ÆSAR (Johnson Matthey, Canada; 99+%) and was recrystallized slowly at room temperature from dilute perchloric acid. The stock solution was prepared by adding the freshly filtered precipitate to a solution of approximately 0.05 molal $HClO_4$. Total uranium in the stock solution was determined gravimetrically using 8-hydroxyquinoline as described by VOGEL (1978). Total perchlorate in the stock solution ($2m_2 + m_3$; where m_2 and m_3 are molalities of uranyl perchlorate and perchloric acid, respectively) was determined by passing weighed aliquots of the solution through an ion exchange resin [Rexyn 101(H)] with titration of the eluent with a standard solution of sodium hydroxide. Excess perchlorate or total perchloric acid in the stock solution was obtained by difference. The stock solution was diluted by weight with a standard solution of approximately 0.05 molal $HClO_4$.

The densities of all solutions were measured relative to water at each of the experimental temperatures with a Sodev 03D vibrating tube densimeter (PICKER *et al.*, 1974) which was calibrated with pure water and a standard solution of NaCl. Densities of the standard NaCl solutions were determined from the data listed by MILLERO (1970). Heat capacities were measured relative to water with a Sodev CP-C Picker type flow microcalorimeter (PICKER *et al.*, 1971). Temperatures were maintained (constant to ± 0.001°C) with separate Sodev CT-L circulating baths and monitored with calibrated thermistors. Daily evaluation of the calorimetric heat loss correction factor (DESNOYERS *et al.*, 1976) by way of measurements on standard solutions of NaCl led to $f = 1.007 \pm 0.001$ at 25°C. This heat loss factor was assumed to be independent of temperature.

11.3 Results

11.3.1 Apparent molar properties

Aqueous solutions containing U(VI) undergo drastic speciation changes with small changes in pH (BAES and MESMER, 1976; LANGMUIR, 1978). Various hydrolyzed species dominate at pH values above 2. At pH values below 2, uranium (VI) is present almost entirely as UO_2^{2+}(aq). At the concentrations of perchloric acid used in these solutions, it was calculated that the hydrolyzed uranium species represent much less than 0.1% of total uranium, and hence are neglected in subsequent calculations.

It was found that apparent molar volumes and heat capacities for solutions containing $UO_2(ClO_4)_2$(aq) and $UO_2(NO_3)_2$(aq) lead to different standard state values for UO_2^{2+}(aq) presumably because of complexation of uranyl with nitrate.

Values for the density and specific heat capacity of pure water at each of the experimental temperatures (KELL, 1967; 1972) are listed in Chapter 4, Table 4.2. The experimentally determined relative densities $(d - d_1^\circ)$ and heat capacity ratios $(c_p d/c_{p,1}^\circ d_1^\circ - 1)$ for all of the aqueous solutions containing $UO_2(ClO_4)_2$ and $HClO_4$ are listed in Table 11.1 at each of the experimental temperatures. The "experimental" apparent molar property ${}^\phi Y^{exptl}$ of a solution is defined generally by

$$ {}^\phi Y^{exptl} = \frac{Y_{soln} - 55.509 Y_1^\circ}{m_2 + m_3} \tag{11.4} $$

where Y_{soln} is the extensive property (volume or heat capacity) of a solution that contains 1 kilogram of solvent (water), Y_1° is the molar volume or heat capacity of pure solvent (water), and m_2 and m_3 are the molalities of $UO_2(ClO_4)_2$ and $HClO_4$, respectively. Experimental apparent molar volumes and heat capacities were calculated from the results listed in Table 11.1 by way of

$$ {}^\phi V^{exptl} = \frac{\frac{1 + m_2 M_2 + m_3 M_3}{d} - \frac{1}{d_1^\circ}}{m_2 + m_3} \tag{11.5} $$

and

$$ {}^\phi C_p^{exptl} = \frac{c_p(1 + m_2 M_2 + m_3 M_3) - c_{p,1}^\circ}{m_2 + m_3} \tag{11.6} $$

where M represents the solute molar mass, c_p and d are the specific heat capacity and density of the solution, and $c_{p,1}^\circ$ and d_1° are the specific heat capacity and density

of pure water. Table 11.1 lists the values of all of these experimental apparent molar volumes and heat capacities.

Because of the presence of perchloric acid in all of these solutions (used to suppress hydrolysis), it is necessary to subtract the contribution this solute makes from the measured properties to obtain properties for the desired solute, $UO_2(ClO_4)_2$. The experimental apparent molar properties of the solutions have been separated into terms representing each of the two solutes using Young's rule (YOUNG and SMITH, 1954; REILLY and WOOD, 1969):

$$^{\phi}Y^{exptl} = \frac{m_2}{m_2 + m_3}\,^{\phi}Y_2 + \frac{m_3}{m_2 + m_3}\,^{\phi}Y_3 + \delta \tag{11.7}$$

Here $^{\phi}Y_2$ and $^{\phi}Y_3$ apply at the total ionic strength of the solution, and δ is an excess mixing term. Because of the large ratio of m_2 to m_3, and the presence of a common anion, it is expected that δ is small enough to ignore in subsequent calculations.

The functional dependence of the apparent molar volumes and heat capacities of $UO_2(ClO_4)_2$ and $HClO_4$ are well represented by extended Debye-Hückel equations of the type

$$^{\phi}Y_2 = \bar{Y}_2^{\circ} + \frac{3}{2}\omega A_Y \left(\frac{1}{\Lambda} - \frac{\sigma}{3}\right) I^{1/2} + B_Y I + C_Y I^{3/2} \tag{11.8}$$

where

$$I = \omega m = \frac{1}{2}\sum m_i z_i^2 \tag{11.9}$$

$$\Lambda = 1 + I^{1/2} \tag{11.10}$$

$$\sigma = \frac{3\left(\Lambda - \frac{1}{\Lambda} - 2\ln\Lambda\right)}{I^{3/2}} \tag{11.11}$$

In these equations $^{\phi}Y_2^{\circ}$ is the standard state (infinite dilution) property, and B and C parameters are concentration dependent terms. Values for the Debye-Hückel limiting slopes (A_Y) were taken from ANANTHASWAMY and ATKINSON (1984) and are listed in Table 11.2.

Apparent molar volumes and heat capacities for $HClO_4$ from 10 to 55°C were taken from Chapter 4. Expressions of the type given by eqs. 11.8-11.11 were fitted to the experimental apparent molar properties in Table 11.1 to generate values of $\bar{Y}_2^{\circ}$, B_Y, and C_Y. It was found that the temperature dependence of the B_V and C_V parameters could be described by quadratic equations of the form

$$B_V(and\ C_V) = p_1 + p_2 T + p_3 T^2 \tag{11.12}$$

Table 11.1: Compositions of solutions and experimental apparent molar volumes and heat capacities for $UO_2(ClO_4)_2/HClO_4$ mixtures.

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	ϕV^{exptl} (cm^{3}mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	ϕC_p^{exptl} (J K^{-1}mol^{-1})
			10°C		
0.4529	0.06480	16.6000	87.529	−4.163	11.72
0.3444	0.06338	12.8436	85.588	−3.320	2.787
0.2711	0.06243	10.2577	83.731	−2.741	−5.912
0.2388	0.06201	9.1071	82.672	−2.470	−8.985
0.1746	0.06117	6.7936	79.629	−1.935	−19.60
0.1258	0.06053	5.0136	76.256	−1.506	−26.65
0.09271	0.06010	3.8008	72.471	−1.202	−32.28
0.05595	0.05962	2.4401	66.042	−0.863	−41.18
			25°C		
0.4529	0.06480	16.3475	91.400	−3.751	61.28
0.3444	0.06338	12.6434	89.578	−3.018	50.19
0.2711	0.06243	10.0963	87.731	−2.488	42.19
0.2388	0.06201	8.9615	86.710	−2.231	40.94
0.1746	0.06117	6.6823	83.645	−1.739	31.67
0.1258	0.06053	4.9318	80.035	−1.351	23.71
0.09271	0.06010	3.7339	76.308	−1.075	18.30
0.05595	0.05962	2.3942	69.594	−0.769	7.36
			40°C		
0.4529	0.06480	16.1182	94.498	−3.632	81.93
0.3444	0.06338	12.4686	92.620	−2.905	72.81
0.2711	0.06243	9.9491	90.959	−2.397	65.37
0.2388	0.06201	8.8364	89.733	−2.150	63.05
0.1746	0.06117	6.5814	86.876	−1.682	53.72
0.1258	0.06053	4.8587	83.018	−1.305	44.83
0.09271	0.06010	3.6721	79.514	−1.040	39.65
0.05595	0.05962	2.3551	72.310	−0.743	26.75

Table 11.1: (continued).

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	ϕV^{exptl} (cm^{3}mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	ϕC_p^{exptl} (J K^{-1}mol^{-1})
			55°C		
0.4529	0.06480	15.9968	95.401	−3.662	80.69
0.3444	0.06338	12.3679	93.667	−2.918	73.17
0.2711	0.06243	9.8750	91.812	−2.387	67.80
0.2388	0.06201	8.7573	91.003	−2.154	65.28
0.1746	0.06117	6.5246	88.012	−1.665	58.98
0.1258	0.06053	4.8156	84.163	−1.296	49.31
0.09271	0.06010	3.6285	81.324	−1.043	44.13
0.05595	0.05962	2.3272	73.883	−0.751	28.27

Table 11.2: Standard state partial molar volumes, heat capacities, and ionic strength parameters for $UO_2(ClO_4)_2(aq)$.*

t (°C)	${}^{\phi}V_2^{\circ}$ (cm^3mol^{-1})	A_V ($cm^3kg^{1/2}mol^{-3/2}$)	B_V ($cm^3kg\ mol^{-2}$)	C_V ($cm^3kg^{3/2}mol^{-5/2}$)
10	89.60 ± 0.27	1.6420	1.872 ± 1.0	-0.8894 ± 0.8
25	94.13 ± 0.15	1.8743	1.440 ± 0.6	-0.9992 ± 0.4
40	97.72 ± 0.54	2.1540	0.0857 ± 2.2	-0.4267 ± 1.6
55	99.09 ± 0.42	2.4946	-2.190 ± 1.5	0.8281 ± 1.1

t (°C)	${}^{\phi}C_{p,2}^{\circ}$ ($JK^{-1}mol^{-1}$)	A_C ($Jkg^{1/2}K^{-1}mol^{-3/2}$)	B_C ($J\ kg\ K^{-1}mol^{-2}$)	C_C ($J\ kg^{3/2}K^{-1}mol^{-5/2}$)
10	-78.1 ± 2	28.446	52.25 ± 8	-21.45 ± 6
25	-7.6 ± 3	32.783	-6.279 ± 11	12.64 ± 8
40	15.8 ± 3	37.446	-12.99 ± 12	11.91 ± 9
55	15.5 ± 3	42.699	-19.70 ± 13	11.17 ± 9

* reported uncertainties were those derived from the fits with unconstrained values of the B_Y and C_Y parameters.

$B_V(10 - 55°C) = -162.91 + 1.162T - 0.002049T^2$

$C_V(10 - 55°C) = 129.18 - 0.8886T + 0.001516T^2$

$B_C(10 - 25°C) = 1171.259 - 3.952T \quad (25 - 55°C) = 127.11 - 0.4474T$

$C_C(10 - 25°C) = -667.976 + 2.2833T \quad (25 - 55°C) = 27.251 - 0.04900T$

$T/K = t/°C + 273.15$

without any loss in the precision of the data fits. The p_i are fitting coefficients and T is the temperature in kelvins. The B_C and C_C parameters that resulted from fits to the measured heat capacities were, however, not adequately represented by expressions of this type. Quadratic and several other types of three parameter expressions led to statistical overfitting of the heat capacity data. The B_C and C_C parameters were accurately represented from 25 to 55 °C by linear equations. Interpolation of the values of these parameters at 25 °C and 10 °C is recommended for intermediate temperatures. The data listed in Table 11.1 were fitted again using the smoothed B and C parameters from 10 to 55 °C for apparent molar volumes and the expressions for these parameters from 25 to 55°C for heat capacities. The results of all of these fits are listed in Table 11.2. The reported fit for heat capacities at 10°C is the original fit using unconstrained B and C parameters.

Plots of ${}^{\phi}Y_2$ minus the Guggenheim form of the Debye-Hückel limiting law (eq. 11.8) are shown in Figures 11.1 and 11.2. The ability of the above described procedure to represent the high concentration behaviour and the standard state values (infinite dilution) is illustrated by these plots.

11.4 Discussion

11.4.1 Standard state properties

Previous measurements on solutions of $UO_2(NO_3)_2$ and UO_2Cl_2 have led to standard state partial molar volumes and heat capacities for UO_2^{2+}(aq). However, all of these studies have neglected consideration of complexation equilibria between UO_2^{2+}(aq) and the anion. Here, measurements on solutions containing perchlorate as the anion are expected to be free of such complications for reasons discussed earlier.

The present $\bar{C}_p^\circ$ and $\bar{V}^\circ$ values listed in Table 11.2, lead to conventional ionic partial molar volumes and heat capacities for UO_2^{2+}(aq) based on $\bar{Y}^\circ(H^+, \text{aq}) \equiv 0$. The conventional ionic properties have been calculated using perchloric acid values from Chapter 4. The results of these calculations are summarized in Table 11.3.

Following procedures described in earlier chapters, modified versions of the equation suggested by HOLMES and MESMER (1983) were used for the representation of the temperature dependence of the standard state heat capacities and volumes of

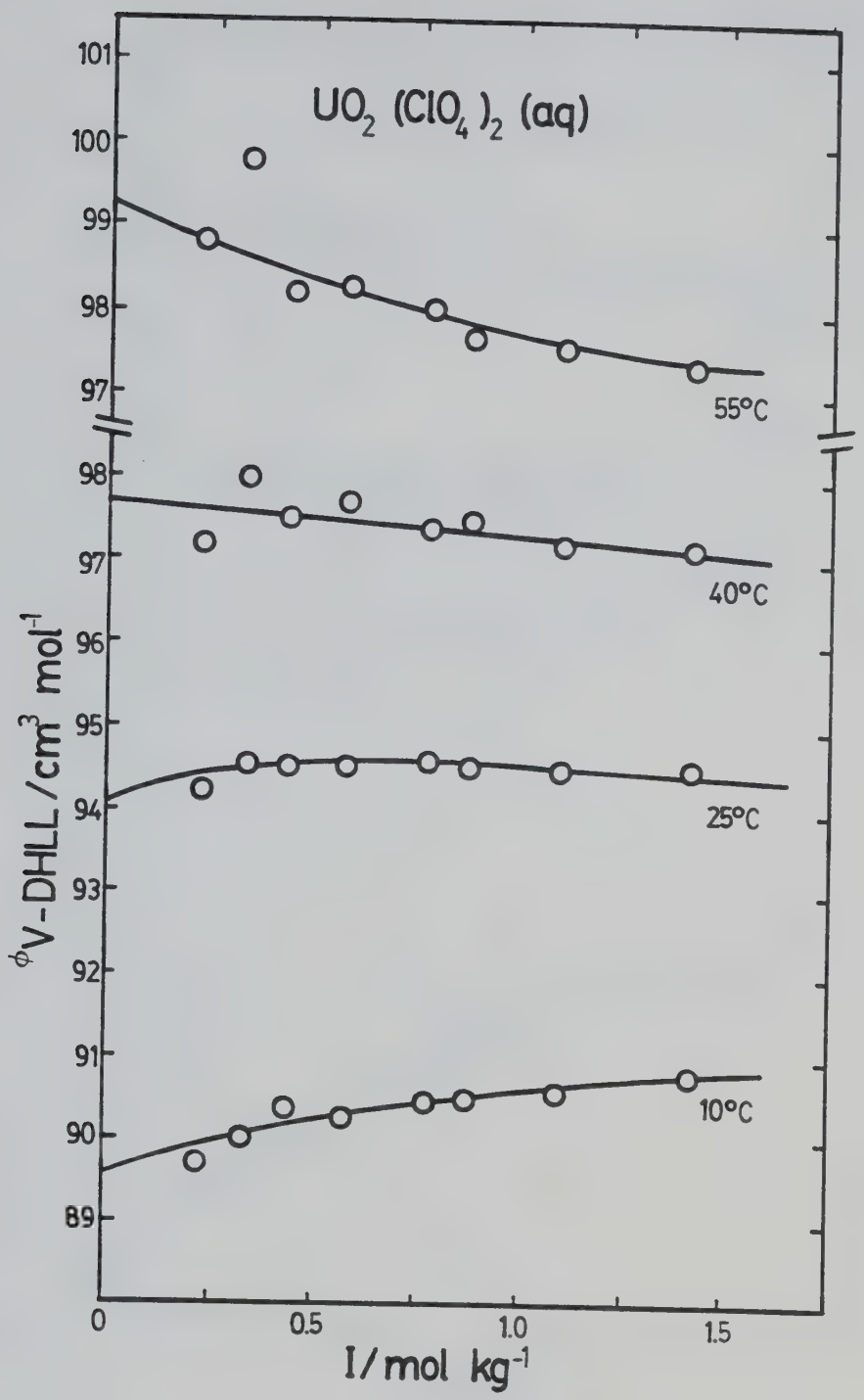

Figure 11.1: Apparent molar volumes of $UO_2(ClO_4)_2$(aq) minus the Debye-Hückel limiting law (DHLL) (eq. 11.8) as a function of ionic strength. The plotted curves are the result of fits using constrained values of the B_V and C_V parameters.

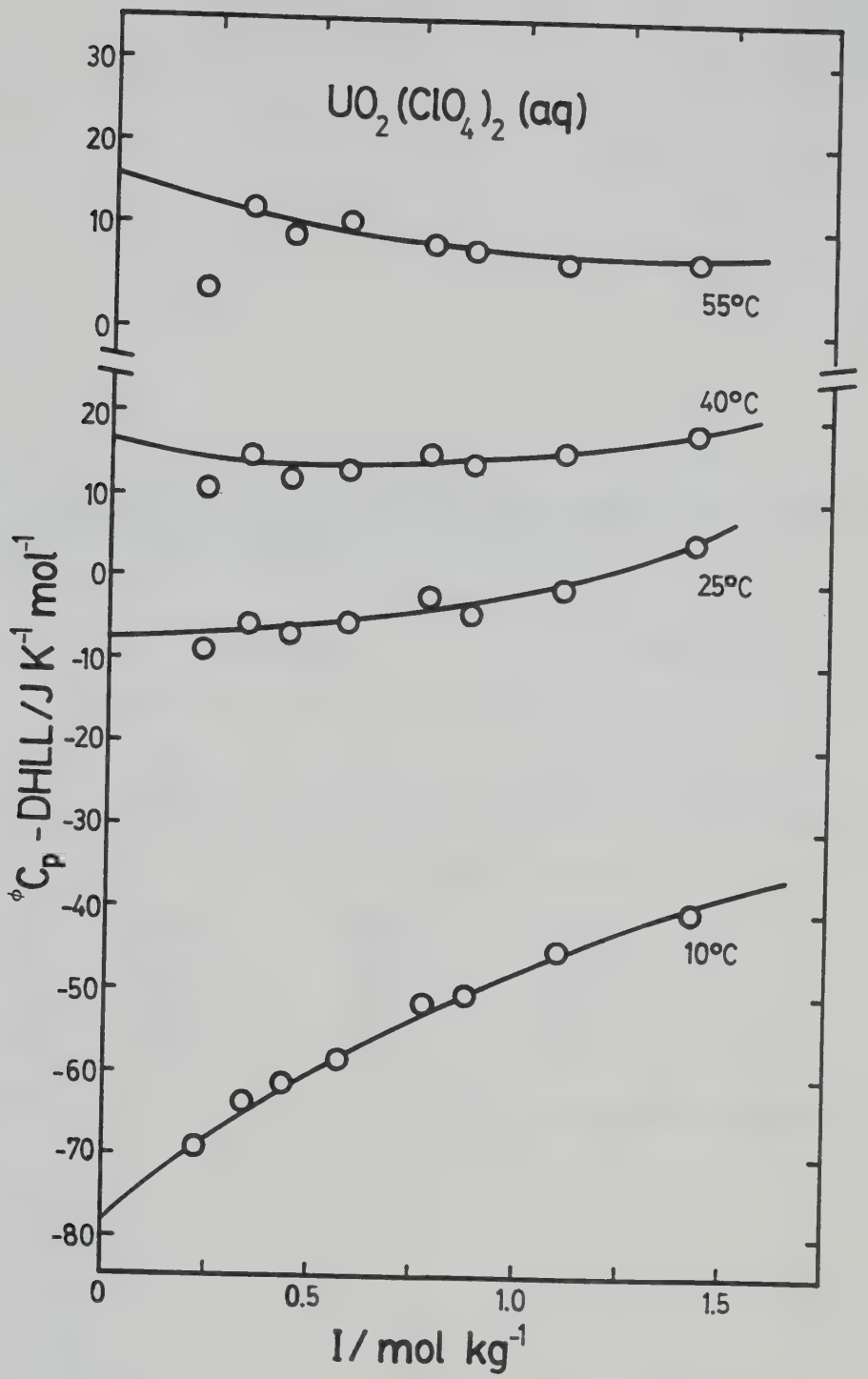

Figure 11.2: Apparent molar heat capacities of $UO_2(ClO_4)_2$(aq) minus the Debye-Hückel limiting law (DHLL) (eq. 11.8) as a function of ionic strength. The plotted curves are the result of fits using constrained values of the B_C and C_C parameters.

Table 11.3: Conventional ionic partial molar volumes and heat capacities for $ClO_4^-(aq)$ and $UO_2^{2+}(aq)$ from 10 to 55°C based on $\bar{Y}°(H^+, aq) \equiv 0$.

	$ClO_4^-(aq)$		$UO_2^{2+}(aq)$	
t (°C)	$\bar{V}°$ (cm^3mol^{-1})	$\bar{C}_p^\circ$ ($JK^{-1}mol^{-1}$)	$\bar{V}°$ (cm^3mol^{-1})	$\bar{C}_p^\circ$ ($JK^{-1}mol^{-1}$)
10	41.63	−62.2	6.3	46
25	44.04	−25.0	6.1	42
40	46.24	−9.0	5.2	34
55	47.31	−5.2	4.5	26

$UO_2(ClO_4)_2$:

$$\bar{Y}_2^\circ = a + \frac{b}{T-\theta} + cT + dT^2 \tag{11.13}$$

Equations of the type given by eq. 11.13 were fitted to the data given in Table 11.2 to generate the following expressions valid from 10 to 55°C:

$$\bar{C}_p^\circ[UO_2(ClO_4)_2,\ aq] = 3166.7 - 7.0256T - \frac{116910}{T-190} \tag{11.14}$$

$$\bar{V}^\circ[UO_2(ClO_4)_2,\ aq] = -296.52 + 2.3555T - 0.0035036T^2 \tag{11.15}$$

Plots of the fitted equations are shown along with the experimental data for $UO_2(ClO_4)_2$ in Figures 11.3 and 11.4.

The following expressions were reported in Chapter 4 to describe the temperature dependence of the standard state heat capacities of $HClO_4$(aq) from 10 to 55 °C and the standard state volumes from 10 to 65 °C:

$$\bar{V}^\circ(HClO_4,\ aq) = -107.79 + 0.87322T - 0.0012203T^2 \tag{11.16}$$

$$\bar{C}_p^\circ(HClO_4,\ aq) = 1408.1 - \frac{55801}{T-190} - 3.0767T \tag{11.17}$$

Combination of the expressions for uranyl perchlorate with those from perchloric acid cited above leads to the following equations for UO_2^{2+}(aq) over the temperature range 10 to 55°C :

$$\bar{V}^\circ(UO_2^{2+},\ aq) = -107.79 + 0.87322T - 0.0012203T^2 \tag{11.18}$$

$$\bar{C}_p^\circ(UO_2^{2+},\ aq) = 350.5 - 0.8722T - \frac{5308}{T-190} \tag{11.19}$$

These expressions are valid over the stated temperature range and should be used in this temperature region rather than other equations that appear in the last section of this Chapter for use at higher temperatures.

11.4.2 Literature comparisons

Several studies have lead to reported standard state partial molar heat capacities for the aqueous uranyl ion at 25 °C. Measurements of the heat capacities of aqueous solutions containing UO_2Cl_2 and $UO_2(NO_3)_2$ have been made by KAPUSTINSKY and LIPILINA (1955). They have reported the values $\bar{C}_p^\circ(UO_2Cl_2,\ aq)$ = -233.5 J $K^{-1}mol^{-1}$ and $\bar{C}_p^\circ[UO_2(NO_3)_2,\ aq] = -129.4$ J $K^{-1}mol^{-1}$. We have recalculated their data using expressions of the type given by eq. 11.8 and have obtained

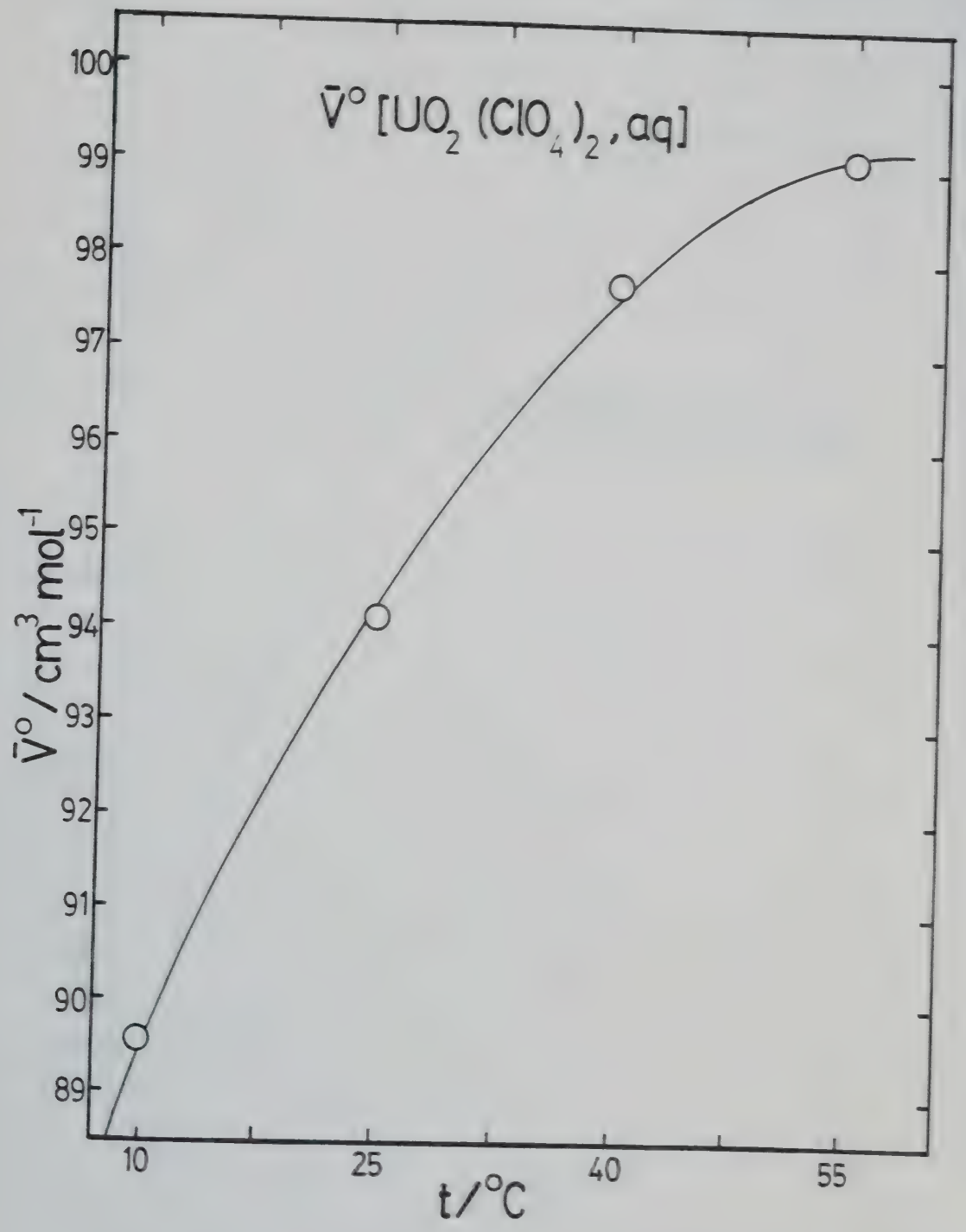

Figure 11.3: Standard state partial molar volumes for $UO_2(ClO_4)_2(aq)$. The solid line is the fit according to eq. 11.15.

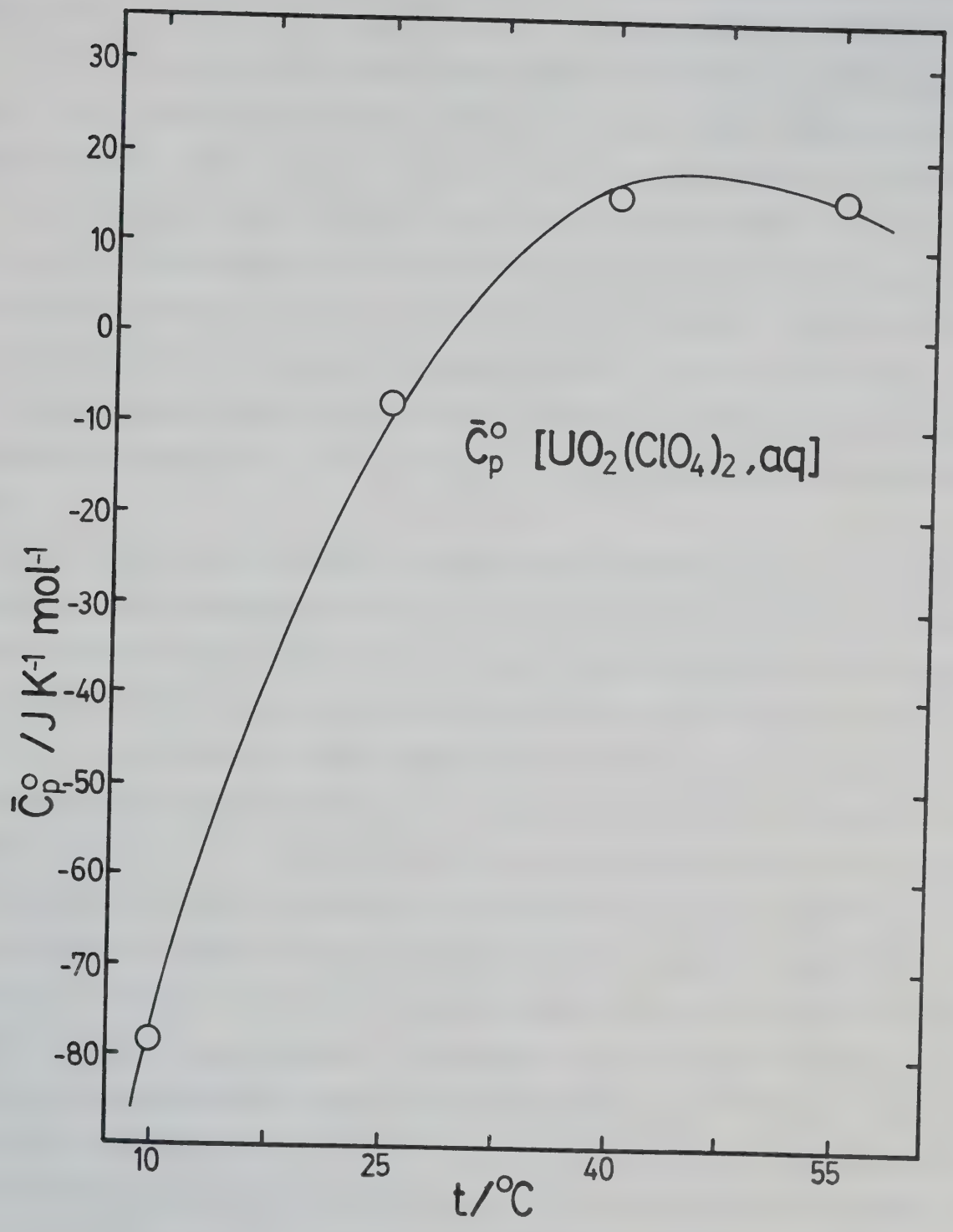

Figure 11.4: Standard state partial molar heat capacities for $UO_2(ClO_4)_2$(aq). The solid line is the fit according to eq. 11.14.

$\bar{C}_p^\circ(UO_2Cl_2, aq)$ = -227 ± 10 J $K^{-1}mol^{-1}$ and -158 < $\bar{C}_p^\circ[UO_2(NO_3)_2, aq]$ < -73 J $K^{-1}mol^{-1}$. The data reported for $UO_2(NO_3)_2$ are only precise enough to justify $\bar{C}_p^\circ[UO_2(NO_3)_2, aq]$ = -116 ± 60 $JK^{-1}mol^{-1}$. These values in combination with the conventional ionic partial molar heat capacities of $Cl^-(aq)$ and $NO_3^-(aq)$ at 25 °C of −126.6 and -72 J $K^{-1}mol^{-1}$ (TREMAINE *et al.*, 1986; Chapter 2) lead to $\bar{C}_p^\circ(UO_2^{2+}, aq)$ = 26 ± 12 and 1 ± 60 J $K^{-1}mol^{-1}$, respectively, from the two salts as compared to the present $\bar{C}_p^\circ(UO_2^{2+}, aq)$ = 42.4 ± 3 J $K^{-1}mol^{-1}$. The probable sources of these discrepancies and large uncertainties are complexation and hydrolysis reactions. Enthalpy of solution measurements of $UO_2(NO_3)_2 \cdot 6H_2O$ from 15 to 45 °C have led DEVINA *et al.* (1982) to report $\bar{C}_p^\circ(UO_2^{2+}, aq)$ = 58.6 ± 0.6 J $K^{-1}mol^{-1}$. This result although quoted with an overly optimistic uncertainty (probably should be equal to or larger than ± 30 J $K^{-1}mol^{-1}$), is in fair agreement with the present value.

Several authors have reported measurements that have led to the densities of aqueous solutions containing aqueous uranyl ion, although only relatively few studies have been done with a high enough precision to permit calculation of the apparent molar volumes. Relatively precise density measurements have been reported by KAPUSTINSKY and LIPILINA (1956). Results from this study were recalculated with an expression of the type given by eq. 11.8, which leads to the value $\bar{V}^\circ[UO_2(NO_3)_2, aq]$ = 65.2 ± 0.2 cm^3mol^{-1}. Combination of this value with the conventional ionic partial molar volume for NO_3^- (Chapter 2) of 29.3 cm^3mol^{-1} leads to $\bar{V}^\circ(UO_2^{2+}, aq)$ = 6.6 ± 0.3 cm^3mol^{-1}, which is in good agreement with the present value $\bar{V}^\circ(UO_2^{2+}, aq)$ = 6.0 ± 0.1 cm^3mol^{-1} calculated using the conventional ionic volume for $ClO_4^-(aq)$ of 44.04 cm^3mol^{-1} from Chapter 2. MANZUROLA and APELBLAT (1985) have made densimetric measurements on aqueous solutions containing $UO_2(NO_3)_2$, UO_2Cl_2, and UO_2SO_4 to very low ionic strengths. They have treated their results assuming negligible hydrolysis and complete dissociation of each salt. From this treatment they have derived the values $\bar{V}^\circ$ = 66.68, 48.05, and 31.86 cm^3mol^{-1} for the three salts based on their results below 0.25 mol kg^{-1} for $UO_2(NO_3)_2$ and UO_2Cl_2 and below 0.04 mol kg^{-1} for UO_2SO_4. These results are all slightly high because of their neglect of the curvature of plots of ${}^\phi V$ versus $m^{1/2}$ due to the effects of both ionic strength and the decrease in ion pair formation as the concentrations of solutions

approach infinite dilution. All of their experimental data have been refitted, which has resulted in new derived values for $\bar{V}°(UO_2^{2+}, aq)$ based on their measurements on solutions containing $UO_2(NO_3)_2$ and UO_2Cl_2. These calculations lead to the values for $\bar{V}°(UO_2^{2+}, aq) = 7.6 \pm 0.2$ and 11.5 ± 0.3 cm^3mol^{-1} respectively, using conventional ionic partial molar volumes for $NO_3^-(aq)$ and $Cl^-(aq)$ as given in Chapter 2 and by ALLRED and WOOLLEY (1981). The discrepancies among these calculated values for $UO_2^{2+}(aq)$ are almost certainly caused by the presence of ion-pairs and hydrolyzed species that also account for the discrepancies in the available heat capacity results.

Calorimetric and densimetric measurements on aqueous solutions containing $UO_2(NO_3)_2$, UO_2Cl_2, and UO_2SO_4 in dilute acid have been determined from 10 to 55 °C (Chapters 12 and 13). It was found that solutions containing $UO_2(NO_3)_2$ are not free of complexation and thus should not give the same standard state properties as the perchlorate results. Calculations involving densimetric and calorimetric measurements on some of the solutions cited above have shown that reasonable agreement is produced once the effects of ion-pair formation and complexation are taken into account.

11.5 Correlations at 25°C

The importance of aqueous ions of the type MO_2^{2+} common for actinide elements, has given rise to many attempts to estimate some of the thermodynamic properties for these ions. Here we consider only methods for the prediction of the standard state heat capacity.

The recent correlation of ABRAHAM and MARCUS (1986) predicts the value $\bar{C}_p°(UO_2^{2+}, aq) = 12$ J $K^{-1}mol^{-1}$ which is in good agreement with the direct value considering the complexity of this ion. The Criss-Cobble entropy correspondence principle (CRISS and COBBLE, 1964a,b) can be used to generate $\bar{C}_p°(UO_2^{2+}, aq) = 12$ J $K^{-1}mol^{-1}$ which is also in good agreement with the present value. Some better (Chapter 3) and less good results from the Criss-Cobble correlation (Chapters 6, 7 and 18) are reported elsewhere in this thesis.

The observed standard state volumes and heat capacities are consistent with

expectations of both electrostatic and non-electrostatic contributions. Monatomic 2+ cations have associated standard state volumes and heat capacities at 25°C of between -17 to -28 cm^3mol^{-1} (MILLERO, 1972) and -6 to -42 J $K^{-1}mol^{-1}$ (Chapter 18), respectively. The observed standard state volumes and heat capacities of UO_2^{2+}(aq) at 25°C of 6.1 cm^3mol^{-1} and 42 J $K^{-1}mol^{-1}$ are comparable to expected values based on the increase in both of these properties due to the size of the cation (non-electrostatic) and the likely decrease in the electrostatic interactions.

11.6 High temperature extrapolations

The Helgeson-Kirkham-Flowers(HKF) semi-theoretical representation (HELGESON and KIRKHAM, 1974, 1976; HELGESON *et al.*, 1981) of standard state thermodynamic properties of aqueous ions is an excellent means by which low temperature thermodynamic data (such as reported here) can be extrapolated to higher temperatures. For example, in Chapter 4 low temperature (10-40°C) heat capacity data for HCl(aq) were extrapolated to over 140°C with extrapolated values agreeing with the best experimental data over the entire temperature range.

The HKF model (HELGESON *et al.*, 1981) gives the following functional forms for the temperature dependence of standard state partial molar volumes and heat capacities of aqueous electrolytes:

$$\bar{V}^\circ = \sigma + \frac{\xi T}{T-\theta} + \Delta V_{Born} \tag{11.20}$$

$$\bar{C}_p^\circ = c_1 + \frac{c_2 T}{T-\theta} + \Delta C_{p,Born} \tag{11.21}$$

In these equations,

$$\Delta V_{Born} = -\omega Q = -\omega \frac{1}{\epsilon}\left(\frac{\partial \ln \epsilon}{\partial p}\right)_T \tag{11.22}$$

and

$$\Delta C_{p,Born} = \omega T X = \omega T \frac{1}{\epsilon}\left[\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_p - \left(\frac{\partial \ln \epsilon}{\partial T}\right)_p^2\right] \tag{11.23}$$

Expressions of these types were fitted to the experimental data for the standard state partial molar volumes and heat capacities given in Table 11.2. In all of these equations the "effective" radii for anionic species are taken equal to crystallographic radii, and for cationic species are taken equal to crystallographic radii plus 0.94 Å.

These effective aqueous radii were calculated from the "effective ionic radii" listed by SHANNON (1976). Values of X and Q were taken from the compilations of HELGESON and KIRKHAM (1974, 1976). The results of the HKF fits to the experimental results reported here, and also the fits to data for $HClO_4$(aq) (required in subsequent calculations) are listed below:

$$\frac{\bar{V}^\circ[UO_2(ClO_4)_2,\ aq]}{cm^3mol^{-1}} = 137.147 - \frac{11.1348T}{T-208} - 10.172 \times 10^6 Q \quad (11.24)$$

$$\frac{\bar{C}_p^\circ[UO_2(ClO_4)_2,\ aq]}{J\ K^{-1}mol^{-1}} = 176.05 - \frac{8.7554T}{T-268.2} - 10.172 \times 10^5 TX \quad (11.25)$$

$$\frac{\bar{V}^\circ(HClO_4,\ aq)}{cm^3mol^{-1}} = 84.508 - \frac{16.465T}{T-167.4} - 4.75415 \times 10^6 Q \quad (11.26)$$

$$\frac{\bar{C}_p^\circ(HClO_4,\ aq)}{J\ K^{-1}mol^{-1}} = 89.43 - \frac{8.6367T}{T-261.0} - 4.75415 \times 10^5 TX \quad (11.27)$$

As can be seen in the above equations, the θ values obtained by fits to the volumetric and heat capacity data are different (as discussed in several earlier Chapters).

These expressions for the partial molar heat capacities and volumes for these species could be used for calculation of the high temperature Gibbs free energies of aqueous uranyl ion. Because of the lack of accurate data at elevated temperatures, these calculations are not presented here. Other calculations involving ionic equilibria with uranyl ion as one participant are presented in the following Chapter.

11.7 References

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Chapter 12

Thermodynamics of complexed aqueous uranyl species I: Volume and heat capacity changes for the formation of the inner-sphere uranyl sulphate complex from 10 to 55°C

12.1 Introduction

As discussed in the previous Chapter, thermodynamic data for aqueous uranium(VI) species are required in a variety of applications. As also mentioned in the preceding Chapter, uranium (VI) can be present in aqueous solution as a variety of different species depending on anions present and on the concentration of hydrogen ion. Most uranium in groundwater, or in solutions containing even small amounts of common anions, is in the form of uranyl cation [UO_2^{2+}(aq)] complexed with one or more anions present [UO_2^{2+}-X^{z-}(aq)]. Of particular importance in this context are the ion-pairs formed with carbonate and sulphate. Several recent studies have focussed on calorimetric measurements on solutions containing these species (ULLMAN *et al.*, 1986; GRENTHE *et al.*, 1986). Substantial interest in uranyl (also other aqueous actinide ion-pairs) comes from the fact that these species are more mobile than the uncomplexed uranyl ion. Thermodynamic properties for these species are required for use in models that calculate speciation and transportation of such uranium(VI) through groundwater.

Many of the applications mentioned above require thermodynamic data (mostly equilibrium constants) at or near room temperature. It has been shown earlier in this thesis that reactions of the type that form ion pairs are non-isocoulombic and thus are expected to have large associated standard state heat capacity changes. Equilibrium constants for reactions with such large heat capacity changes are expected to be strongly temperature dependent, and subsequently not accurately calculated at

temperatures more than a few degrees away from the temperature of measurement with the standard state enthalpy change. For these reasons and the desire to predict equilibrium constants for these types of reactions at even higher temperatures, apparent molar heat capacities and volumes of aqueous solutions containing UO_2SO_4 and H_2SO_4 were determined from 10 to 55°C. Small amounts of acid are required in solutions containing uranyl ion because of its tendancy for hydrolysis (BAES and MESMER, 1976).

The available equilibrium data (SMITH and MARTELL, 1976) suggest that almost all of the aqueous uranyl and sulphate ions are present as the neutral ion-pair $UO_2SO_4(aq)$. The presence of sulphuric acid in all of the solutions under present investigation ensures that even a larger fraction of the uranyl ions are present as the ion-paired species. There are, however, several complications associated with the following treatment because of the presence of small amounts of completely dissociated uranyl and sulphate ions. The use of sulphuric acid to prevent hydrolysis of the uranium ions also presents additional complications because of the bisulphate-sulphate equilibrium (discussed in Chapter 4). As mentioned earlier in several Chapters, the intentional temperature shift required for heat capacity measurements alters amounts of species present in solution, with degrees of such compositional changes depending on the magnitude of the enthalpy change associated with the reaction. Because these solutions contain uranyl sulphate in sulphuric acid, and because there are two coupled equilibria present in these solutions, the resulting calculations are complex. Another example of a system containing coupled equilibria was discussed in Chapter 5 with reference to Cr(VI).

12.2 Experimental

Water used for all experiments was first passed through an activated charcoal filter and then through a Milli-RO4/Milli-Q reagent grade mixed bed ion exchange and activated carbon system to yield purified water with a resistivity of 18 MΩ cm or greater. Solutions of NaCl (Fisher certified, ACS) were prepared by mass after drying the salt at 110 °C until constant weight.

Uranyl sulphate was obtained from Alfa (+96%) and was recrystallized several

times from dilute sulphuric acid. Concentrated sulphuric acid was obtained from Fisher (certified, ACS). The stock solution of uranyl sulphate was prepared by adding the purified salt to a sulphuric acid solution of approximately 0.05 molal. Total uranium in the stock solution was determined gravimetrically using 8-hydroxyquinoline as described by VOGEL (1978). The total anion concentration in the stock solution ($2m_2 + m_3$; where m_2 and m_3 are the stoichiometric molalities of uranyl sulphate and sulphuric acid, respectively) was determined by passing weighed aliquots of the solution through an ion exchange resin [Rexyn 101(H)] and titrating the eluent with a standard solution of sodium hydroxide. Since the solutions investigated here contain mostly the uranyl sulphate ion-pair, widely varying amounts of stock solution were passed through the ion exchange columns. The total amount of anionic concentration in the solution was found to be independent of amount, thus indicating complete exchange. The amount of excess sulphuric acid in the stock solution was obtained by difference. The stock solution was diluted by mass with a standard solution of sulphuric acid with molality equal to approximately 0.05.

The densities of all solutions were measured relative to water at each of the experimental temperatures ± 0.01 °C with a Sodev 03D vibrating tube densimeter (PICKER *et al.*, 1974), which was calibrated with pure water and a standard solution of NaCl. Densities of the standard NaCl solutions were obtained from the data listed by MILLERO (1970). Heat capacities were measured relative to water with a Sodev CP-C Picker type flow microcalorimeter (PICKER *et al.*, 1971). Temperatures were maintained (constant to ± 0.001°C) with separate Sodev CT-L circulating baths and monitored with calibrated thermistors. Daily evaluation of the calorimetric heat loss correction factor (DESNOYERS *et al.*, 1976) by way of measurements on standard solutions of NaCl led to $f = 1.006 \pm 0.001$ at 25°C. This heat loss factor was assumed to be independent of temperature.

12.3 Results

12.3.1 Experimental apparent molar properties

As mentioned in the Introduction, at low pH values and high concentrations of uranyl and sulphate ions, most of the U(VI) is present as the ion-paired or complexed

species $[UO_2SO_4(aq)]$. At higher concentrations of sulphate ion, the di-sulphate complex $[UO_2(SO_4)_2^{2-}]$ may be present (SMITH and MARTELL, 1976). At high pH values a variety of monomeric and polymeric uranium-hydroxy species may also be present (BAES and MESMER, 1976; LANGMUIR, 1978) and in the presence of sulphate ion mixed complexes may be formed. In an attempt to reduce many of these complications, the measurements described here were performed on solutions containing sufficient acid to permit neglect of hydrolyzed species. Also, a relatively small excess of sulphuric acid was used in an attempt to avoid formation of higher sulphate complexes.

"Experimental" apparent molar properties (${}^{\phi}Y^{exptl}$) of solutions containing two electrolytes are defined generally by

$$ {}^{\phi}Y^{exptl} = \frac{Y_{soln} - 55.509Y_1^{\circ}}{m_2 + m_3} \tag{12.1} $$

where Y_{soln} is the extensive property (volume or heat capacity) of a solution that contains 1 kilogram of solvent (water), Y_1° is the molar volume or heat capacity of pure solvent (water), and m_2 and m_3 are the stoichiometric molalities of uranyl sulphate and sulphuric acid. Specific equations for calculations of these defined quantities are the following:

$$ {}^{\phi}V^{exptl} = \frac{\frac{1 + m_2M_2 + m_3M_3}{d} - \frac{1}{d_1^{\circ}}}{m_2 + m_3} \tag{12.2} $$

$$ {}^{\phi}C_p^{exptl} = \frac{c_p(1 + m_2M_2 + m_3M_3) - c_{p,1}^{\circ}}{m_2 + m_3} \tag{12.3} $$

In these equations M represents the solute molar mass, c_p and d are the specific heat capacity and density of the solution, and $c_{p,1}^{\circ}$ and d_1° are the specific heat capacity and density of pure water.

Values for the density and specific heat capacity of pure water at each of the experimental temperatures (KELL, 1967; 1972) are listed in Chapter 4, Table 4.2. The experimentally determined relative densities $(d - d_1^{\circ})$ and heat capacity ratios $(c_p d/c_{p,1}^{\circ} d_1^{\circ} - 1)$ along with calculated "experimental" apparent molar properties for all of the aqueous solutions containing UO_2SO_4 and H_2SO_4 are listed in Table 12.1.

The two equilibria of present interest are represented by the following equations:

$$ UO_2^{2+}(aq) + SO_4^{2-}(aq) = UO_2SO_4(aq) \tag{12.4} $$

Table 12.1: Compositions of solutions and experimental apparent molar volumes and heat capacities for UO_2SO_4 and H_2SO_4 mixtures.

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	ϕV^{exptl} (cm^{3}mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	ϕC_p^{exptl} (J K^{-1}mol^{-1})
			10°C		
0.8725	0.6606	30.0568	41.906	−4.768	35.94
0.5008	0.3998	18.0559	39.454	−3.255	7.37
0.3766	0.3127	13.8380	38.381	−2.640	−5.07
0.2500	0.2238	9.4169	37.172	−1.917	−17.97
0.1800	0.1747	6.9385	35.912	−1.486	−28.52
0.1313	0.1406	5.1824	35.066	−1.153	−33.73
0.09635	0.1161	3.9111	34.132	−0.9046	−38.02
0.07272	0.09947	3.0526	32.938	−0.7292	−41.72
0.06591	0.09469	2.8018	32.652	−0.6772	−42.07
			25°C		
0.8725	0.6606	29.6598	43.725	−3.895	68.16
0.5008	0.3998	17.7875	41.724	−2.531	51.19
0.3766	0.3127	13.623	40.828	−1.996	44.88
0.2500	0.2238	9.3322	38.451	−1.412	32.54
0.1800	0.1747	6.8234	38.607	−1.055	34.03
0.1313	0.1406	5.0937	37.822	−0.7970	33.01
0.09635	0.1161	3.8405	36.990	−0.6059	33.17
0.07272	0.09947	2.9881	36.244	−0.4744	34.38
0.06591	0.09469	2.7401	36.065	−0.4374	35.02
			40°C		
0.8725	0.6606	29.2651	45.308	−3.470	86.07
0.5008	0.3998	17.5362	43.568	−2.159	75.86
0.3766	0.3127	13.4234	42.816	−1.676	72.23
0.2500	0.2238	9.1113	42.150	−1.148	70.83
0.1800	0.1747	6.7114	40.941	−0.8466	67.88
0.1313	0.1406	5.0107	40.101	−0.6293	67.84
0.09635	0.1161	3.7742	39.388	−0.4709	69.25
0.07272	0.09947	2.9285	39.021	−0.3591	73.45
0.06591	0.09469	2.6897	38.542	−0.3291	73.06

Table 12.1: (continued).

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	ϕV^{exptl} (cm^{3}mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	ϕC_p^{exptl} (J K^{-1}mol^{-1})
			55°C		
0.8725	0.6606	29.1624	45.111	−3.177	92.75
0.5008	0.3998	17.4608	43.454	−1.958	84.04
0.3766	0.3127	13.3651	42.693	−1.484	82.68
0.2500	0.2238	9.0690	42.073	−1.026	80.44
0.1800	0.1747	6.6616	41.370	−0.747	80.53
0.1313	0.1406	4.9708	40.620	−0.552	81.04
0.09635	0.1161	3.7431	39.944	−0.411	82.47
0.07272	0.09947	2.9019	39.713	−0.311	87.15
0.06591	0.09469	2.6549	39.872	−0.282	89.97

$$HSO_4^-(aq) = H^+(aq) + SO_4^{2-}(aq) \qquad (12.5)$$

Calculations with appropriate equilibrium constants for each of the experimental temperatures must first be done before further calculations with the "experimental" apparent molar properties can be completed. For analysis of results from the heat capacity measurements, the contribution due to "chemical relaxation" must also be considered. Details of literature selections, speciation calculations, and chemical relaxation calculations are described in detail in the following sections.

12.3.2 Selections of literature data

Several authors have reported equilibrium constants at room temperature for the reaction represented by eq. 12.4. Most of the available data have been summarized in several reviews and compilations (SILLÉN and MARTELL, 1964; SILLÉN and MARTELL, 1971; SMITH and MARTELL, 1976; HÖGFELDT, 1982; FUGER *et al.*, in prep.). Values reported for the equilibrium constant at zero ionic strength and 25°C range from 580 to 8500 for reaction 12.4 (DAVIES and MONK, 1957; ALLEN, 1958; BROWN *et al.*, 1954; WALLACE, 1967; MAJCHRZAK, 1973; NIKOLAEVA, 1971, 1976). It appears that the "best" values for the equilibrium constant are around 1400. We chose to refit the data reported by WALLACE (1967) and AHRLAND and KULLBERG (1971) to extended Debye-Hückel equations of the form

$$\log Q = \log K - \frac{8A_\gamma I^{1/2}}{1 + B_\gamma \text{å}\ I^{1/2}} + BI \qquad (12.6)$$

Values for A_γ and B_γ were taken from ROBINSON and STOKES, 1959 and å (7.0 Å) was taken from WALLACE (1967). Values for log K and B obtained from these fits are listed for 25°C (and other temperatures from calculations described later) in Table 12.2. It should be noted that the results of both AHRLAND and KULLBERG (1971) and WALLACE (1967) were obtained for solutions with compositions expressed as molarity, and as such all appropriate parameters in eq. 12.6 pertain to molarity.

Several authors have reported enthalpies for uranyl sulphate complexation, some by way of dlnK/dT and some by way of calorimetry. The enthalpies determined by way of calorimetric measurements are preferred here. BAILEY and LARSON (1971) have obtained $\Delta H^\circ = 20.8_4$ kJ mol^{-1} and ULLMAN *et al.* (1986) have obtained ΔH° = 19.6 kJ mol^{-1}, both at zero ionic strength. AHRLAND and KULLBERG (1971)

Table 12.2: Equilibrium constant expressions for uranyl sulphate complexation from 10 to 55°C.*

$t/(°C)$	A_γ	B_γ	$\log K$
10	0.4989	0.3264	
25	0.5115	0.3291	3.185
40	0.5262	0.3323	
55	0.5432	0.3358	

Note that all of these coefficients pertain to solutions of known molarity. For units of A_γ and B_γ see ROBINSON and STOKES (1954). The listed values can be used without regard to units if å is in angstroms.

have derived $\Delta H = 18.23$ kJ mol^{-1} at an ionic strength of one molar. Although the measurements of BAILEY and LARSON (1971) are considered more reliable, they were averaged with the result from ULLMAN *et al.* (1986) who used equilibrium data more in accord with the present selections. This average value was combined with results from AHRLAND and KULLBERG (1971) to obtain

$$\Delta H/(\text{kJ mol}^{-1}) = 20.21 - 1.979I \tag{12.7}$$

for 25°C and ionic strengths less than approximately one molar.

Thermodynamic data for sulphuric acid that are required in all calculations of speciation and relaxation were taken from PITZER *et al.* (1977) as reported in Chapter 4. The two reactions of interest can be written in terms of fractional extents of reaction (for convenience in later calculations of relaxation contributions) as in the following:

$$\begin{array}{ccccc} \mathrm{UO_2^{2+}(aq)} & + & \mathrm{SO_4^{2-}(aq)} & = & \mathrm{UO_2SO_4(aq)} \\ (1-\alpha)m_2 & & (1-\alpha)m_2+\beta m_3 & & \alpha m_2 \end{array} \tag{12.4}$$

$$\begin{array}{ccccccc} \mathrm{HSO_4^-(aq)} & = & \mathrm{H^+(aq)} & + & \mathrm{SO_4^{2-}(aq)} \\ (1-\beta)m_3 & & (1+\beta)m_3 & & (1-\alpha)m_2+\beta m_3 \end{array} \tag{12.5}$$

The molalities of ionic species to be used in the Pitzer equations that follow can be expressed in terms of α and β. The pertinent equations from PITZER *et al.* (1977) are listed below.

The activity coefficient ratio for the bisulphate-sulphate equilibrium ($\gamma_{H^+}\gamma_{SO_4^{2-}}$ / $\gamma_{HSO_4^-}$), which is denoted by γ_2 (here the two main equilibrium reactions represented by eqs. 12.4 and 12.5 will henceforth be denoted as system "1" and "2" respectively), has the form (PITZER *et al.*, 1977)

$$\begin{aligned} \ln\gamma_2 = {} & 4f^\gamma - 4\beta m_3 B_{H1} + 2[(1-\alpha)m_2 + (1+2\beta)m_3]\beta^{(0)}_{H2} + \\ & 2(1+\beta)m_3[2(1-\alpha)m_2 + (1+3\beta)m_3]C_{H2} + 4m_3^2(1-\beta^2)B_{H1'} \end{aligned} \tag{12.8}$$

in which certain quantities are defined by

$$f^\gamma = -A_\phi\left[\frac{I^{1/2}}{1+1.2I^{1/2}} + \frac{2\ln(1+1.2I^{1/2})}{1.2}\right] \tag{12.9}$$

$$B_{H1} = \beta_{H1}^{(0)} + \frac{\beta_{H1}^{(1)}[1 - (1 + 2I^{1/2}) \exp(-2I^{1/2})]}{2I} \tag{12.10}$$

$$B_{H1'} = \frac{\beta_{H1}^{(1)}[-1 + (1 + 2I^{1/2} + 2I) \exp(-2I^{1/2})]}{2I^2} \tag{12.11}$$

Here $\beta_{H1}^{(0)}$, $\beta_{H1}^{(1)}$, $\beta_{H2}^{(0)}$, and $C_{H2} = C_{H2}^{\phi}/2^{3/2}$ are all constants that are independent of ionic strength but dependent on temperature as in the following:

$$\beta_{H1}^{(0)} = 0.05584 + \frac{46.040}{T} \tag{12.12}$$

$$\beta_{H1}^{(1)} = -0.65758 + \frac{336.514}{T} \tag{12.13}$$

$$\beta_{H2}^{(0)} = -0.32806 + \frac{98.607}{T} \tag{12.14}$$

$$C_{H2}^{\phi} = 0.25333 - \frac{63.124}{T} \tag{12.15}$$

The equilibrium constant is given by (Chapter 4)

$$\ln K_2 = -4.5563 + 2825.2\left(\frac{1}{T} - \frac{1}{298.15}\right) - 31.81\left[\ln\left(\frac{T}{298.15}\right) - 1 + \left(\frac{298.15}{T}\right)\right] \tag{12.16}$$

In principle the speciation of all of the solutions can now be calculated by using Newton's method to solve the various ionic equilibria equations. These resulting concentrations of species could then be used for calculations of apparent molar volumes, but further analyses of the shift in this speciation with temperature is required before calculations of apparent molar heat capacities can be completed. The specific details of the speciation calculations will be deferred until after the discussion of chemical relaxation.

12.3.3 Relaxation calculations

Detailed accounts of chemical relaxation in relation to heat capacities of aqueous solutions have been presented in Chapters 4 and 5 and also will be presented in Chapter 16. The discussions in Chapters 4 and 16 are particularly relevant to the discussion here. For systems containing several species connected by coupled equilibria such as reported here and in Chapter 5, the total heat capacity contribution

from chemical relaxation is given by

$$ {}^{\phi}C_{p,tot}^{rel} = \Delta H_1 \left(\frac{\partial \alpha}{\partial T}\right)_{p,m_2} + \Delta H_2 \left(\frac{\partial \beta}{\partial T}\right)_{p,m_3} \tag{12.17} $$

where ΔH_1 and ΔH_2 correspond to the first and second pertinent equilibria (1 for uranyl sulphate comlexation, and 2 for the dissociation of bisulphate ion), and all ΔH values are those at the total ionic strength of the specific solution under study. The challenge in these types of calculations is in the derivation of appropriate expressions for $(\partial\alpha/\partial T)_{p,m_2}$ and $(\partial\beta/\partial T)_{p,m_3}$. The expressions derived in Chapter 4 for solutions of pure sulphuric acid are relatively complicated, but become more complicated in the present case because this reaction is coupled to the uranyl sulphate complexation reaction. The following series of equations represent $(\partial\alpha/\partial T)_{p,m_2}$ and $(\partial\beta/\partial T)_{p,m_3}$:

$$ Q_1 = \frac{\alpha}{(1-\alpha)[(1-\alpha)m_2 + \beta m_3]} \tag{12.18} $$

$$ K_2 = \frac{(1+\beta)[(1-\alpha)m_2 + \beta m_3]\gamma_2}{1-\beta} \tag{12.19} $$

$$ f_1 = 1 + m_2(1-\alpha)Q_1 + Q_1 f_2 + 4m_2(1-\alpha) f_2 \left(\frac{\partial Q_1}{\partial I}\right)_{T,p} \tag{12.20} $$

$$ f_2 = (1-\alpha)m_2 + \beta m_3 \tag{12.21} $$

$$ f_3 = (1+\beta)[2(1-\alpha) + (1+3\beta)m_3] \tag{12.22} $$

$$ f_4 = f_2(1-\beta)\gamma_2 \tag{12.23} $$

$$ \left(\frac{\partial \alpha}{\partial T}\right)_{p,m} = \frac{e\left(\frac{\partial \beta}{\partial T}\right)_{p,m} + g}{f} \tag{12.24} $$

$$ \left(\frac{\partial \beta}{\partial T}\right)_{p,m} = \frac{ag + f(c-d)}{fb - ae} \tag{12.25} $$

$$ a = m_2\gamma_2(1+\beta) - f_4\left[-16m_2\left(\frac{\partial f^{\gamma}}{\partial I}\right)_{T,p} + 16m_2m_3\beta\left(\frac{\partial B_{H1}}{\partial I}\right)_{T,p} - 2m_2\beta_{H2}^{(0)} - 4m_2m_3C_{H2}(1+\beta) - 16m_2m_3^2(1-\beta^2)\left(\frac{\partial B_{H1'}}{\partial I}\right)_{T,p}\right] \tag{12.26} $$

$$ b = K_2 + m_3\gamma_2(1+\beta) + f_2\gamma_2 + f_4\left[8m_3\left(\frac{\partial f^{\gamma}}{\partial I}\right)_{T,p} - 8m_3^2\beta\left(\frac{\partial B_{H1}}{\partial I}\right)_{T,p} - 4m_3B_{H1} + 4m_3\beta_{H2}^{(0)} + 6m_3^2C_{H2} + 2m_3C_{H2}\left(\frac{f_3}{1+\beta}\right) + \right. $$

$$8m_3^3(1-\beta^2)+\left(\frac{\partial B_{H1'}}{\partial I}\right)_{T,p}-8m_3^2\beta B_{H1'}\Bigg] \tag{12.27}$$

$$c = (1-\beta)K_2\left(\frac{\partial \ln K_2}{\partial T}\right)_p \tag{12.28}$$

$$d = f_4\left\{4\left(\frac{\partial f^\gamma}{\partial T}\right)_{p,I}-4\beta m_3\left(\frac{\partial B_{H1}}{\partial T}\right)_{p,I}+2\left(\frac{\partial \beta_{H2}^{(0)}}{\partial T}\right)_p[(1-\alpha)m_2+ (1+2\beta)m_3]+2m_3f_3\left(\frac{\partial C_{H2}}{\partial T}\right)_p+4m_3^2(1-\beta^2)\left(\frac{\partial B_{H1'}}{\partial T}\right)_{p,I}\right\} \tag{12.29}$$

$$e = m_3Q_1(1-\alpha)+2m_3(1-\alpha)f_2\left(\frac{\partial Q_1}{\partial I}\right)_{p,T} \tag{12.30}$$

$$f = 1+m_2(1-\alpha)Q_1+Q_1f_2+4m_2(1-\alpha)f_2\left(\frac{\partial Q_1}{\partial I}\right)_{p,T} \tag{12.31}$$

$$g = (1-\alpha)f_2\left(\frac{\partial Q_1}{\partial T}\right)_{p,I} \tag{12.32}$$

Q_1 was used instead of K_1 and γ_1 for calculations involving uranyl sulphate because of the availability of $Q_1 = f(I)$.

As can be seen in the above equations, for quantities such as γ_2 and Q_1 that depend both on ionic strength and temperature, the applicable derivative for relaxation calculations can be obtained from the total differential of these functions:

$$g = g(I,T,p) \tag{12.33}$$

$$dg = \left(\frac{\partial g}{\partial I}\right)_{T,p}dI+\left(\frac{\partial g}{\partial T}\right)_{I,p}dT+\left(\frac{\partial g}{\partial p}\right)_{T,I}dp \tag{12.34}$$

Since pressure is constant the last term in this equation is equal to zero. Dividing through by dT and imposing constant pressure leads to

$$\left(\frac{\partial g}{\partial T}\right)_p = \left(\frac{\partial g}{\partial I}\right)_{T,p}\left(\frac{\partial I}{\partial T}\right)_p+\left(\frac{\partial g}{\partial T}\right)_{I,p} \tag{12.35}$$

The ionic strength in solutions containing uranyl sulphate and sulphuric acid is given by

$$I = 4(1-\alpha)m_2+(1+2\beta)m_3 \tag{12.36}$$

Thus

$$\left(\frac{\partial g}{\partial T}\right)_p = \left(\frac{\partial g}{\partial T}\right)_{I,p} + \left[-4m_2\left(\frac{\partial \alpha}{\partial T}\right)_p + 2m_3\left(\frac{\partial \beta}{\partial T}\right)_p\right]\left(\frac{\partial g}{\partial I}\right)_{T,p} \tag{12.37}$$

These equations were used in evaluation of derivatives of Q_1 and also for other derivatives required for evaluation of relaxation corrections for sulphuric acid as given in Chapater 4.

The special case of chemical relaxation in solutions containing several solutes is treated in detail in Chapter 16. This discussion does not, however, consider the case of mixed aqueous electrolytes with coupled equilibria. The extension to these systems is straightforward. The total contribution from chemical relaxation to the "exptl" apparent molar heat capacities has the form

$${}^{\phi}C_{p,\Sigma}^{rel} = \frac{m_2}{m_2+m_3}\Delta H_1\left(\frac{\partial \alpha}{\partial T}\right)_{p,m_2} + \frac{m_3}{m_2+m_3}\Delta H_2\left(\frac{\partial \beta}{\partial T}\right)_{p,m_3} \tag{12.38}$$

It should be noted that all m_2 and m_3 values cited thus far refer to the stoichiometric molalities of uranyl sulphate and sulphuric acid. Henceforth, these will be denoted $m_{2,i}$ and $m_{3,i}$ distinguishing them from equlibrium molalities as defined in the next section.

12.3.4 Speciation calculations

The speciations of all of these solutions at 25°C were calculated using the above expressions in combination with mass and charge balance equations and Newton's method for solving equations. The calculation scheme involved two steps, each step iterated ten times, and the overall sequence about ten times. Initially α and β were estimated (ignoring activity coefficients) from data for solutions of the pure solutes in water. The ionic strength was also estimated from these values and converted to molar ionic strength for use in several of the equations given above. First the parameters for sulphuric acid (γ_2) were calculated, which were then used in calculations of total speciation. The results were found to converge quickly and the large number of iterations employed here led to differences in calculated α or β values of less than 10^{-10} between the 9th and 10th iterations.

The results of these speciation calculations were used along with the following analysis to obtain the standard state partial molar heat capacity of UO_2SO_4(aq) at

25°C. As mentioned earlier, the reaction of uranyl ion with sulphate has a large heat capacity change (here a value of 168 J $K^{-1}mol^{-1}$ was calculated from data presented in the next section and in Chapters 4 and 18). Refinement of the equilibrium constant expression and enthalpy changes for uranyl sulphate with the heat capacity cited later at 25°C leads to the equations

$$\begin{aligned} \log K_1 &= 3.1850 - 1055.65\left(\frac{1}{T} - \frac{1}{298.15}\right) - 9.146\left[\ln\left(\frac{T}{298.15}\right) - 1 + \right. \\ &\quad \left.\left(\frac{298.15}{T}\right)\right] \\ \Delta H_1^\circ &= 20.21 + 0.175(T - 298.15) \quad \text{kJ mol}^{-1} \end{aligned} \tag{12.38}$$

These expressions were used for subsequent evaluation of the amounts of species present and in the relaxation calculations. The results of these speciation calculations are given along with the contributions from chemical relaxation (calculated with these refined equations) in Table 12.3.

12.3.5 Apparent molar properties of UO_2SO_4

The tabulated "experimental" apparent molar properties listed in Table 12.1 contain contributions from all species present and from chemical relaxation (for heat capacities). The heat capacity measurements have been "corrected" to "species properties" for the solutions by subtracting the contribution due to chemical relaxation.

The experimental apparent molar properties of the solutions can be separated into terms representing each of the species present in the solution using Young's rule[1] (YOUNG and SMITH, 1954)

$$^{\phi}Y^{exptl} = \sum_{i=2}^{n} \frac{m_i}{\sum_{i=2}^{n} m_i} {}^{\phi}Y_i + \delta \tag{12.39}$$

(12.40)

Here all $^{\phi}Y_i$ values apply at the *total* ionic strength of the solution, m_i are equilibrium molalities of (m_2: UO_2^{2+}, SO_4^{2-}), (m_3: H^+, HSO_4^-), (m_4: UO_2SO_4), and (m_5: $2H^+$, SO_4^{2-}), and δ is an excess mixing term. The magnitude of δ is expected to be

[1]Strictly speaking the original "experimental" properties that apply in Young's rule are those defined in terms of each of the equilibrium molalities m_2, m_3, m_4, and m_5. However, since $m_{2,i} + m_3 = m_2 + m_3 + m_4 + m_5$, these values are the same.

Table 12.3: Compositions, speciation, ionic strengths, and contributions from chemical relaxation for solutions containing UO_2SO_4 and H_2SO_4.

$m_{2,i}$ (mol kg^{-1})	$m_{3,i}$ (mol kg^{-1})	α	β	I (mol kg^{-1})	${}^{\phi}C_{p,\Sigma}^{rel}$ (J K^{-1}mol^{-1})	${}^{\phi}C_{p}^{exp} - {}^{\phi}C_{p,\Sigma}^{rel}$ (J K^{-1}mol^{-1})
			10°C			
0.87249	0.66064	0.90385	0.24923	1.3255	73.40	−37.46
0.50081	0.39984	0.89073	0.24434	0.8141	73.16	−65.79
0.37659	0.31268	0.88349	0.24807	0.6433	74.08	−79.15
0.24997	0.22384	0.87290	0.2599	0.4673	76.49	−94.46
0.17998	0.17473	0.86445	0.27398	0.3681	79.28	−107.80
0.13133	0.14059	0.85651	0.29021	0.2976	82.60	−116.33
0.09635	0.11605	0.84899	0.30777	0.2457	86.43	−124.45
0.07272	0.09947	0.84248	0.32423	0.2098	90.32	−132.04
0.06591	0.09469	0.84031	0.32996	0.1993	91.75	−133.82
			25°C			
0.87249	0.66064	0.91266	0.14910	1.1625	73.12	−4.96
0.50081	0.39984	0.90039	0.14637	0.7164	73.76	−22.57
0.37659	0.31268	0.89398	0.15026	0.5664	75.37	−30.49
0.24997	0.22384	0.88488	0.16170	0.4113	79.08	−46.54
0.17998	0.17473	0.87787	0.17516	0.3239	83.12	−49.09
0.13133	0.14059	0.87137	0.19078	0.2618	87.82	−54.81
0.09635	0.11605	0.86528	0.20781	0.2162	93.15	−59.98
0.07272	0.09947	0.86005	0.22392	0.1847	98.52	−64.14
0.06591	0.09469	0.85830	0.22955	0.1755	100.49	−65.47
			40°C			
0.87249	0.66064	0.91639	0.06808	1.0424	61.28	24.79
0.50081	0.39984	0.90473	0.06542	0.6430	63.43	12.43
0.37659	0.31268	0.89891	0.06854	0.5078	65.78	6.45
0.24997	0.22384	0.89095	0.07831	0.3679	70.54	0.29
0.17998	0.17473	0.88493	0.09016	0.2891	75.46	−7.58
0.13133	0.14059	0.87950	0.10423	0.2332	81.04	−13.20
0.09635	0.11605	0.87447	0.11985	0.1922	87.28	−18.03
0.07272	0.09947	0.87019	0.13485	0.1641	93.50	−20.05
0.06591	0.09469	0.86876	0.14014	0.1558	95.78	−22.72

Table 12.3: (continued)

$m_{2,i}$ (mol kg^{-1})	$m_{3,i}$ (mol kg^{-1})	α	β	I (mol kg^{-1})	${}^{\phi}C_{p,\Sigma}^{rel}$ (J K^{-1}mol^{-1})	${}^{\phi}C_{p}^{exp} - {}^{\phi}C_{p,\Sigma}^{rel}$ (J K^{-1}mol^{-1})
			55°C			
0.87249	0.66064	0.91628	0.00730	0.9625	45.51	47.24
0.50081	0.39984	0.90486	0.00337	0.5931	48.53	35.51
0.37659	0.31268	0.89935	0.00528	0.4676	51.10	31.58
0.24997	0.22384	0.89203	0.01289	0.3376	56.00	24.44
0.17998	0.17473	0.88667	0.02284	0.2643	60.91	19.62
0.13133	0.14059	0.88191	0.03509	0.2125	66.41	14.63
0.09635	0.11605	0.87758	0.04905	0.1746	72.52	9.95
0.07272	0.09947	0.87392	0.06272	0.1486	78.59	8.56
0.06591	0.09469	0.87270	0.06759	0.1411	80.82	9.15

slightly smaller here than for measurements on solutions containing only uranyl and perchlorate ions (as described in the previous chapter) due to the large amount of complexed uranyl sulphate that should not have strong interactions with other ions in the solutions. Therefore δ was set equal to zero in all subsequent calculations. The relationship of these equilibrium molalities to the stoichiometric concentrations of uranyl sulphate and sulphuric acid are given below:

$$m_2 = (1-\alpha)m_{2,i} \tag{12.41}$$

$$m_3 = (1-\beta)m_{3,i} \tag{12.42}$$

$$m_4 = \alpha m_{2,i} \tag{12.43}$$

$$m_5 = (1-\alpha)m_{2,i} + \beta m_{3,i} \tag{12.44}$$

The apparent molar properties of neutral solutes in water are satisfactorily represented by polynomial expressions of the type

$$^{\phi}Y_4 = \bar{Y}_4^{\circ} + B_Y I + C_Y I^2 \tag{12.44}$$

where $\bar{Y}_4^{\circ}$ is the standard state partial molar property (equal to the apparent molar property at infinite dilution), and B_Y and C_Y are concentration dependent parameters. Expressions for the apparent molar volumes and heat capacities for all of the other solutes present in these solutions are also required. Apparent molar volumes and heat capacities of the species ($2H^+$, SO_4^{2-}) were estimated from two different schemes, the first at 25°C, and the second for other temperatures (as discussed in Chapter 4):

$$25°C: \quad {}^{\phi}Y(2H^+, SO_4^{2-}) = {}^{\phi}Y(2K^+, SO_4^{2-}) - 2{}^{\phi}Y(K^+, Cl^-) + 2{}^{\phi}Y(H^+, Cl^-) \tag{12.45}$$

$$10,40,55°C: \quad {}^{\phi}Y(2H^+, SO_4^{2-}) = {}^{\phi}Y(2Na^+, SO_4^{2-}) - 2{}^{\phi}Y(Na^+, Cl^-) + 2{}^{\phi}Y(H^+, Cl^-) \tag{12.46}$$

At 25°C, volumetric and heat capacity expressions of the general type corresponding to fitting non-extended Debye-Hückel equations to experimental data for K_2SO_4 were taken from Chapter 2, heat capacity expressions were taken directly from DESNOYERS *et al.* (1976) for KCl and HCl, the apparent molar volume data from FORTIER *et al.* (1974) were refit to these same types of expressions, and finally volumetric

data for HCl were taken from ALLRED and WOOLLEY (1981). Volumetric properties for NaCl and Na_2SO_4 were calculated from the parameters in CONNAUGHTON *et al.* (1986), for HCl the values from ALLRED and WOOLLEY (1981) were used for 10 and 40°C, and the expression from HERRINGTON *et al.* (1985) was used at 55°C. Heat capacity expressions applicable at 10, 40, and 55°C for NaCl were derived from PITZER *et al.* (1984), for HCl from Tremaine et al. (1986), and for Na_2SO_4 from ROGERS and PITZER (1981).

Apparent molar volume and heat capacity expressions for completely dissociated uranyl sulphate (UO_2^{2+}, SO_4^{2-}) were derived using the following scheme:

$$\begin{aligned} {}^{\phi}Y(UO_2^{2+},\ SO_4^{2-}) \ = \ & {}^{\phi}Y(UO_2^{2+},\ 2ClO_4^-) - 2{}^{\phi}Y(H^+,\ ClO_4^-) + \\ & {}^{\phi}Y(2H^+,\ SO_4^{2-}) \end{aligned} \tag{12.47}$$

Expressions for uranyl perchlorate and perchloric acid for each of the required temperatures were taken from Chapters 11 and 4, respectively. The expressions for ${}^{\phi}Y(2H^+,\ SO_4^{2-})$ resulted from the scheme described above. Expressions for (H^+, HSO_4^-) were taken from Chapter 4.

Fitting expressions of the type given by eqs. 12.39 and 12.44 to the data given in Tables 12.1 and 12.3 resulted in definition of the limiting standard state properties $\bar{Y}_4^\circ$ and concentration dependent parameters B_Y and C_Y. It was found that the temperature dependences of B_J and C_J parameters were accurately represented and those of B_V and C_V less accurately by linear equations in temperature

$$B_V(\text{and } C_V) = p_1 + p_2 T \tag{12.48}$$

without significant loss in the overall standard deviations of the data fits. In this equation, p_i are fitting coefficients and T is the temperature in kelvins. Each data point was weighted as the inverse square of its estimated standard deviation as given in Table 12.4. The results of fitting the data by the same procedure above using smoothed B and C parameters from eq. 12.48 are reported in Table 12.4. The $\pm$ values assigned to each of the parameters correspond to standard deviations from fits with unconstrained B and C parameters.

Plots of ${}^{\phi}Y_4$ against ionic strength are shown in Figures 12.1 and 12.2.

Table 12.4: Standard state partial molar volumes, heat capacities, and ionic strength parameters for $UO_2SO_4(aq)$.*

t (°C)	$\bar{V}^\circ$ ($cm^3 mol^{-1}$)	B_V ($cm^3 kg\ mol^{-2}$)	C_V ($cm^3 kg^{3/2} mol^{-5/2}$)
10	39.47 ± 0.39	13.57 ± 1.4	-4.20 ± 0.9
25	40.92 ± 0.13	12.36 ± 0.5	-3.68 ± 0.4
40	43.63 ± 0.29	11.15 ± 1.3	-3.17 ± 1.1
55	43.02 ± 0.50	9.93 ± 2.4	-2.65 ± 2.1

t (°C)	$\bar{C}_p^\circ$ ($JK^{-1} mol^{-1}$)	B_C ($J\ kg\ K^{-1} mol^{-2}$)	C_C ($J\ kg^{3/2} K^{-1} mol^{-5/2}$)
10	-140.1 ± 1.2	182.22 ± 4	-42.67 ± 3
25	-70.4 ± 1.0	150.94 ± 4	-38.30 ± 3
40	-1.7 ± 2.1	106.41 ± 9	-27.88 ± 7
55	50.9 ± 1.6	88.39 ± 7	-29.57 ± 6

* Reported uncertainties were those derived from the fits with unconstrained values of the B_Y and C_Y parameters.

$B_V(10 - 55°C) = 36.442 - 0.08078T$
$C_V(10 - 55°C) = -13.984 + 0.03455T$
$B_C(10 - 55°C) = 772.62 - 2.0851T$
$C_C(10 - 55°C) = -125.07 + 0.29101T$
$T/K = t/°C + 273.15$

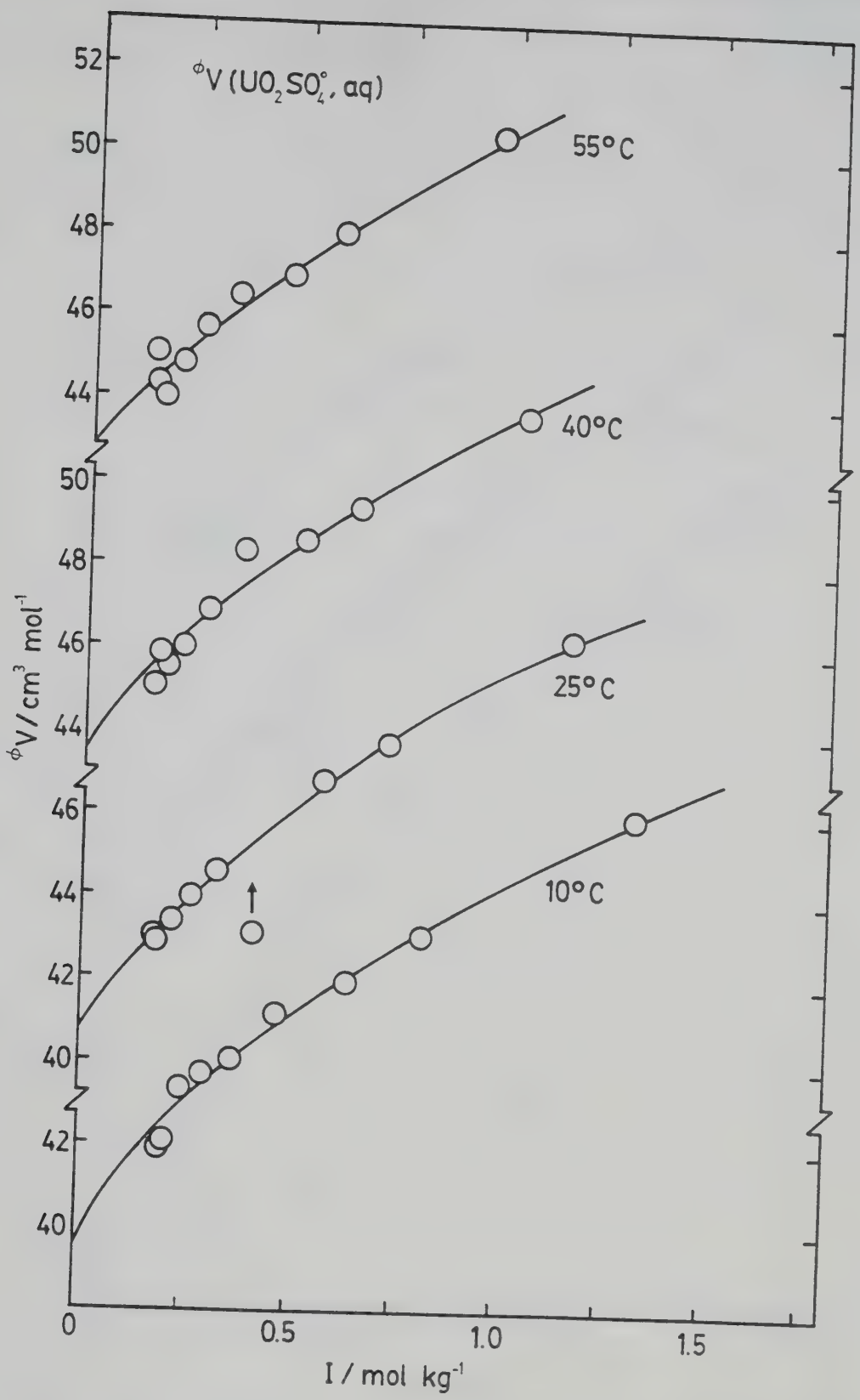

Figure 12.1: Apparent molar volumes of UO_2SO_4(aq) as a function of ionic strength. The plotted curves are the result of fits using constrained values of the B_V and C_V parameters.

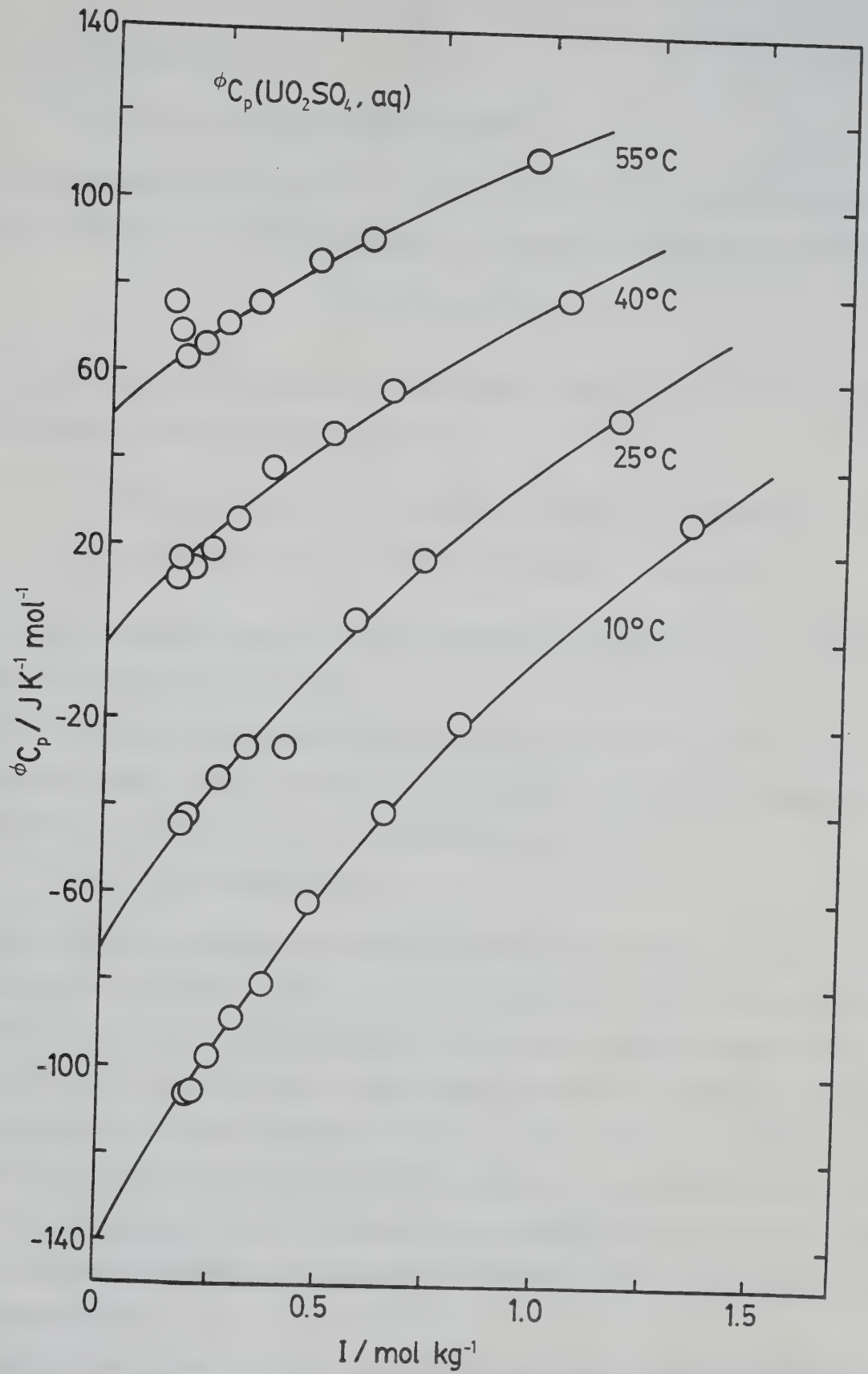

Figure 12.2: Apparent molar heat capacities of UO_2SO_4(aq) as a function of ionic strength. The plotted curves are the result of fits using constrained values of the B_C and C_C parameters.

12.4 Discussion

12.4.1 Standard state properties to 55°C

The temperature dependences of the presently derived standard state volumes and heat capacities are well represented by polynomial expressions of the type

$$\bar{Y}^\circ = a + bT + cT^2 \tag{12.49}$$

Equations of type 12.49 were fitted to the data given in Table 12.3 to obtain the following expressions valid from 10 to 55°C:

$$\bar{V}^\circ(UO_2SO_4,\ aq) = -93.868 + 0.77839T - 0.0010925T^2 \tag{12.50}$$

$$\bar{C}_p^\circ(UO_2SO_4,\ aq) = -2773.10 + 13.636T - 0.015322T^2 \tag{12.51}$$

These standard state volumes and heat capacities are plotted along with the fitted equations in Figures 12.3 and 12.4.

Equilibrium calculations involving uranyl sulphate from 10 to 55°C should employ these results rather than the less accurate equations that permit extrapolation to much higher temperatures that are described later.

12.4.2 Literature comparisons

Although several studies have reported the densities of aqueous solutions containing uranyl sulphate, only the measurements by MANZUROLA and APELBLAT (1985) are of sufficient precision for the calculation of apparent molar properties. Their study however, considered neither the complexation reaction of uranyl with sulphate or the effects of hydrolysis on aqueous uranyl ion. These results are consistent with the present results once these effects have been taken into account. Because the present research was designed from the beginning to permit the best possible analysis in terms of these complications, it is believed that the presently derived properties are the best available.

There do not appear to be any results that can lead to the standard state heat capacity of uranyl sulphate (SMITH-MAGOWAN and GOLDBERG, 1979).

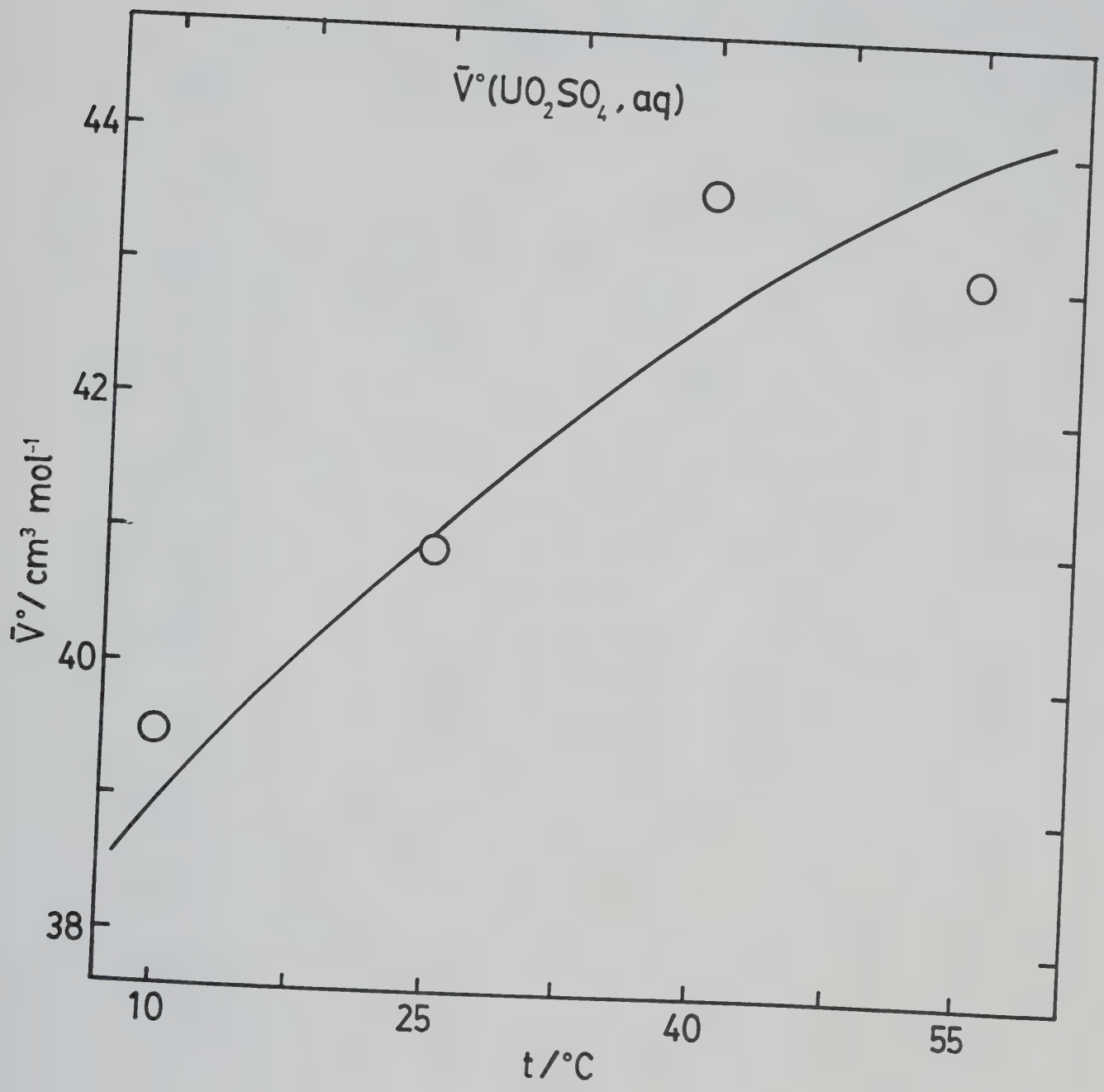

Figure 12.3: Standard state volumes for (UO_2SO_4, aq) from 10 to 55°C.

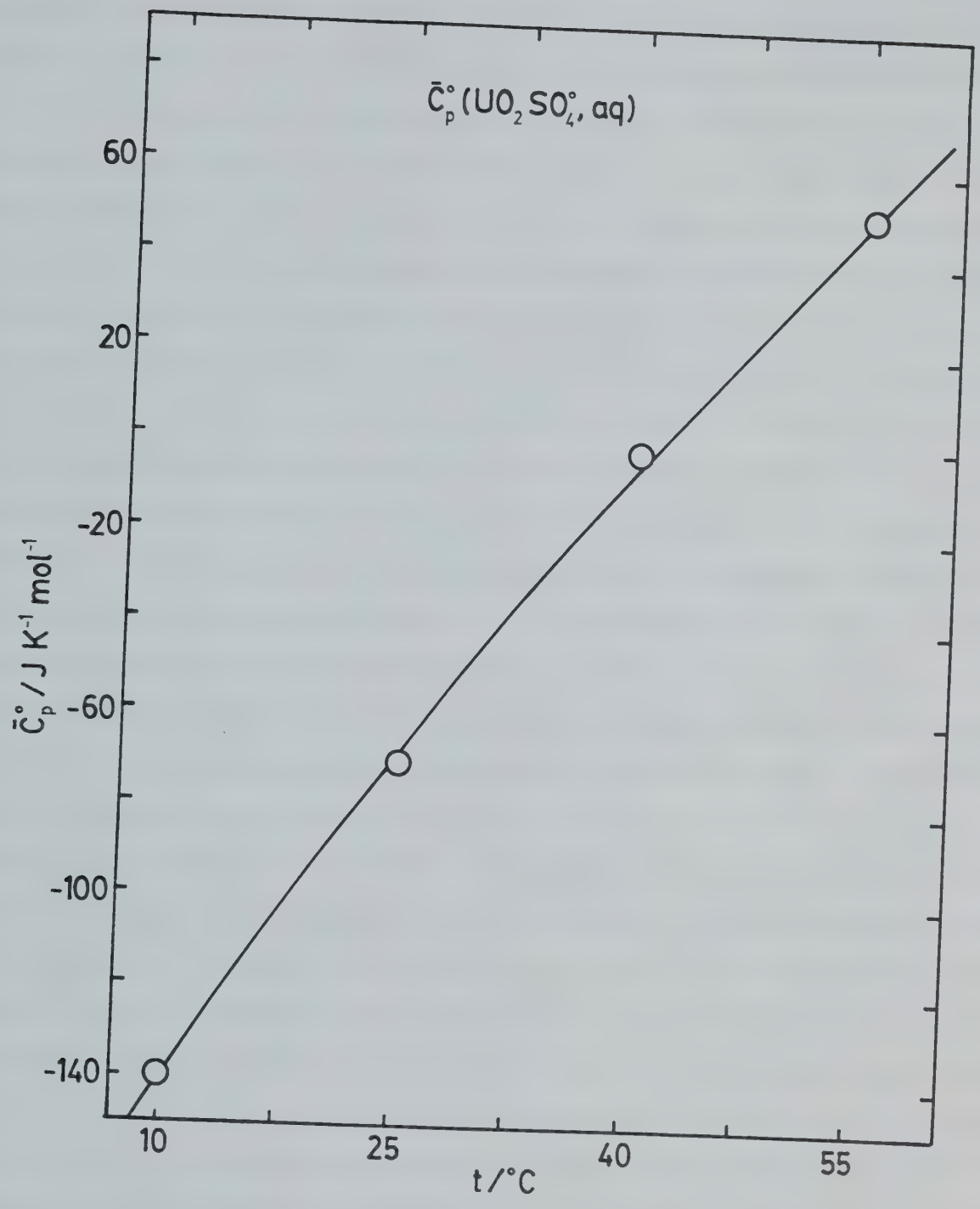

Figure 12.4: Standard state heat capacities for (UO_2SO_4, aq) from 10 to 55°C.

12.4.3 High temperature behaviour

Heat capacities and volumes of hydrophobic neutral solutes such as argon (BIGGERSTAFF *et al.*, 1985) approach $+\infty$ as the critical point of water is approached, whereas the heat capacities of hydrophilic solutes such as all ionic species and several neutral solutes [for example $B(OH)_3$ as described in Chapter 8 or the present UO_2SO_4] are expected to head toward $-\infty$ as the critical point of water is approached. Recent results for the partial molar volumes of boric acid to high temperatures support this claim (GRANT-TAYLOR and READ, 1988). A qualitative approach to the prediction of the high temperature dependence of neutral solutes can be based on the magnitude of the standard state heat capacities near room temperature. Aqueous argon has a standard state heat capacity of over 200 J $K^{-1}mol^{-1}$ at 298 K wheras boric acid and uranyl sulphate have substantially lower values. The electron-rich oxygen ligands in these latter solutes provide potential H–bonding sites for discrete water molecules. As discussed later, the standard state heat capacities of HIO_3(aq) and $MgSO_4$(aq) are also comparably small. An elegant study of the heats of solution of several neutral solutes has been done by OLOFSSON *et al.* (1984) from which can be calculated standard state heat capacities for He(aq), Ne(aq), Ar(aq), Kr(aq), and Xe(aq) of approximately 156, 166, 221, 241, and 271 J $K^{-1}mol^{-1}$, respectively. Values for normal alkanes from C_1 to C_4 show an increase in the standard state heat capacities from 278 to 477 J $K^{-1}mol^{-1}$. It is apparent from much of the theoretical work into the properties of fluids and multicomponent fluids [see for example the elegant discussion by WHEELER (1972) using the decorated lattice-gas model] that the divergent nature of thermodynamic properties of a solute nearing the critical point of the solvent can be qualitatively described in relation to the divergent compressibility (volumes) or in terms of the divergent partial molar enthalpy (heat capacities). Solutes that attract solvent molecules strongly will have associated standard state volumes and heat capacities that tend to $-\infty$ as the critical temperature of the solvent is approached , and those that exhibit only weak attractions or repulsions will diverge to $+\infty$ as is the case for argon. It is clear that heat capacities of solutes (as or more hydrophobic than argon) will diverge positively and solutes (as or more hydrophilic than boric acid) will approach -∞ at temperatures increasing toward the

critical temperature of water. UO_2SO_4(aq) is expected to be in this latter class of solutes.

The Helgeson–Kirkham–Flowers equations of state for the standard state volumes and heat capacities of aqueous solutes have the forms (HELGESON *et al.*, 1981):

$$\bar{V}^\circ = \sigma + \frac{\xi T}{T - \theta} + \Delta V_{Born} \tag{12.52}$$

$$\bar{C}_p^\circ = c_1 + \frac{c_2 T}{T - \theta} + \Delta C_{p,Born} \tag{12.53}$$

Here σ, ξ, c, and θ terms are fitting coefficients dependent on the specific solute. The ΔY_{Born} terms come directly from the relationship of the change in the free energy given by the Born equation to the changes in partial molar volumes and heat capacities as shown by

$$\Delta V_{Born} = -\omega Q \tag{12.54}$$

$$\Delta C_{p,Born} = \omega T X \tag{12.55}$$

where Q and X are the derivatives in pressure and temperature of the dielectric constant [Chapter 4 and HELGESON *et al.* (1981)], ω is given by

$$\omega = \frac{\eta z^2}{r_{eff}} \tag{12.56}$$

and η is a constant equal to 6.9466×10^5 Å J mol^{-1} (HELGESON *et al.* , 1981). For neutral solutes there is no contribution to standard state properties from the Born equation because of the lack of ionic charge.

The HKF model has been modified by TANGER and HELGESON (1988) (but not considered here) and also added to by SHOCK (1987) to include more specifically the divergent nature of the standard state volumes and heat capacities of neutral solutes approaching the critical point of water. Shock has introduced "effective" Born coefficients for aqueous neutral solutes that produce positive ω values (boric acid, uranyl sulphate) or negative ω values (noble gases, hydrocarbons) and subsequently these ω terms accurately fit either the positively or negatively divergent behaviour.

It is apparent from the available heat capacity results (BIGGERSTAFF *et al.*, 1985; BIGGERSTAFF, 1986) that the partial molar heat capacities of hydrophobic solutes begin to head rapidly toward $+\infty$ at $t \approx 300$°C. HKF equations without the

Born terms were fit to the present results with the knowledge that calculations using resultant expressions would be limited to temperatures below 300°C. This approach was deemed more appropriate than estimation of ω values to be used for such fits.

The results of fitting equations of type 12.52 and 12.53 to the results in Table 12.4 (with ω=0) for uranyl sulphate led to the equations given below.

$$\frac{\bar{V}^\circ(UO_2SO_4,\ aq)}{cm^3mol^{-1}} = 51.520 - \frac{2.5400T}{T - 224.2} \tag{12.57}$$

$$\frac{\bar{C}_p^\circ(UO_2SO_4,\ aq)}{J\ K^{-1}mol^{-1}} = 5016.70 - \frac{4028.332T}{T - 62.0} \tag{12.58}$$

Several authors have reported the temperature dependence of the uranyl sulphate complexation reaction over reasonably wide temperature ranges (NIKOLAEVA, 1971, 1976; LIETZKE and STOUGHTON, 1960). None of these results are in good agreement with others presumably due to experimental difficulties. It is of some interest to compare the equilibrium constants that can be calculated from the extrapolated equations cited above with those from the direct results.

The complexation of uranyl ion by sulphate can be represented in terms of the following electrolytes (all totally dissociated *except* uranyl sulphate):

$$UO_2(ClO_4)_2 + Na_2SO_4 + 2HCl = UO_2SO_4 + 2HClO_4 + 2NaCl \tag{12.59}$$

Expressions that result from fitting HKF equations to data for $UO_2(ClO_4)_2$ and $HClO_4$ were reported in Chapters 11 and 4, respectively. Gibbs free energies for Na_2SO_4 were calculated from the heat capacity results from ROGERS and PITZER (1981) combined with room temperature results of DESNOYERS *et al.* (1976), and volumetric data from CONNAUGHTON *et al.* (1986). The former data are applicable in the range 5 to 200°C, and were shown to be consistent to 280°C by PITZER and MURDZEK (1982). The latter results were fitted by HKF expressions of the type given by eq. 4.83 for use above their range of measurement (0 to 100°C). Equilibrium data for NaCl to 300°C were taken from PITZER *et al.* (1984), and Gibbs free energies for HCl were calculated from HKF fits to the heat capacities of HCl(aq) from 10 to 140°C from TREMAINE *et al.* (1986), and fits to the volumetric data from HERRINGTON *et al.* (1985) and ALLRED and WOOLLEY (1981).

Values of the Gibbs free energies and standard state entropies for the participating species in reaction 12.59 were selected as follows. Both free energies and

entropies for ClO_4^-(aq), Na^+(aq), Cl^-(aq), and SO_4^{2-}(aq) were conveniently taken from the NBS tables (WAGMAN *et al.*, 1982). Values for UO_2^{2+}(aq) were taken from FUGER and OETTING (1976). The selected values for the equilibrium constant and enthalpy of reaction of uranyl sulphate complexation that were cited earlier were used along with data for uranyl and sulphate ions to generate $\Delta G^\circ_{f,298}$ = -1715.4 ± 3 kJ mol^{-1} and $\bar{S}^\circ_{298}$ = 51.8 ± 4 J K^{-1}mol^{-1} for UO_2SO_4(aq). All of the selected values for pertinent ionic and neutral species are listed in Table 12.5.

The Gibbs free energy of formation of a species can be calculated over all temperatures and pressures, referenced to the elements in their standard states at 298.15 K and 1 bar, according to

$$\Delta G^\circ_T = \Delta G^\circ_{f,298} - \bar{S}^\circ_{298}(T - 298.15) + \int_{298}^{T} \bar{C}^\circ_p dT - T\int_{298}^{T} \frac{\bar{C}^\circ_p}{T} dT + \int_1^p \bar{V}^\circ dp \quad (12.60)$$

where $\bar{S}^\circ_{298}$ is equal to the standard state partial molar entropy of the species at 298.15 K and 1 bar. The free energies for species not cited above were calculated from expressions of type 12.60. The change in the Gibbs free energy for the reaction represented by eq. 12.4 at temperature and pressure T and p was calculated from these Gibbs free energies for the individual species. The standard state changes in the logarithim of the equilibrium constant of uranyl sulphate complexation were calculated from 0 to 200° from the equations and data cited above in combination with the Lewis equation

$$\log K = \frac{-\Delta G^\circ}{RT\ln(10)} \quad (12.61)$$

The results of these calculations are shown in graphical form along with the direct experimental data in Figure 12.5. There is qualitative agreement with all data sets yet not good agreement with any one set. From the present results and other results cited in Figure 12.5, it is clear that more experimental work is required to unambiguosly define the equilibrium properties of uranyl sulphate solutions even over moderate temperature ranges.

12.4.4 Inner/outer-sphere complexes

There have been many spectroscopic and thermodynamic investigations of the formation of metal sulphate ion pairs or complexes (see for example AHRLAND, 1972;

Table 12.5: Selected thermodynamic properties at 25°C.

Species	$\Delta G^\circ_{f,298}$ (kJ mol^{-1})	$\bar{S}^\circ_{298}$ (J K^{-1}mol^{-1})
$UO_2^{2+}(aq)$	−952.7	−97.1
$UO_2SO_4(aq)$	−1715.4	51.8
$Na^+(aq)$	−261.905	59.0
$Cl^-(aq)$	−131.228	56.5
$ClO_4^-(aq)$	−8.52	182.0
$SO_4^{2-}(aq)$	−744.53	20.1
$H^+(aq)$	0	0

Sources of these values are discussed in the text.

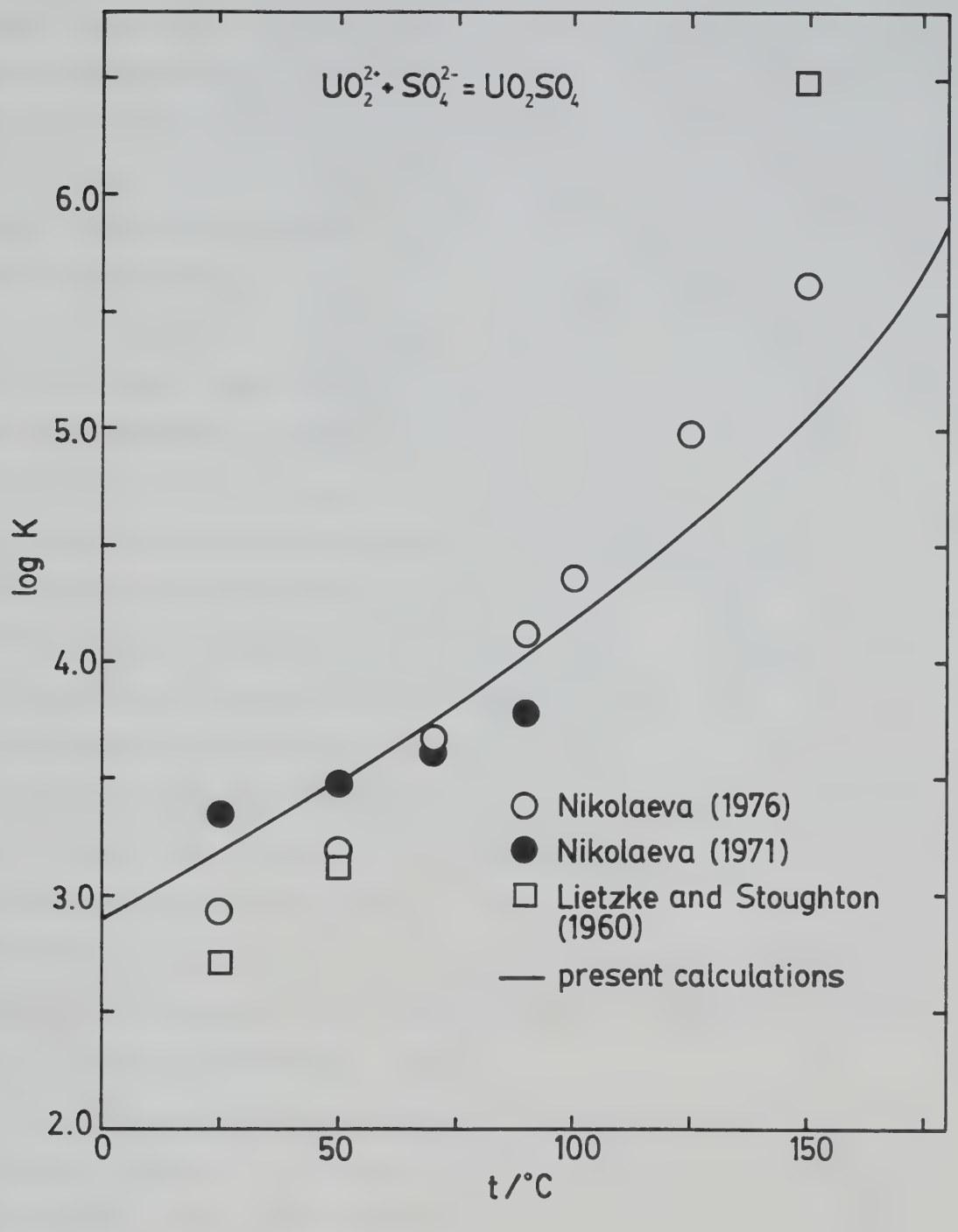

Figure 12.5: Comparison of equilibrium constants for the association of uranyl sulphate from direct experimental results, and predictions from extrapolations of the present results from 10 to 55°C.

LARSSON, 1964; LARSON, 1970,1971; LOSURDO and MILLERO, 1981). The thermodynamic properties of these types of ion pair formation reactions strongly support normal classifications. The first type of reactions are those forming inner-sphere complexes (sometimes labelled contact ion-pairs), and the second type are those that form outer-sphere complexes (solvent separated ion-pairs). Characteristic of inner-sphere complexes is the displacement of inner sphere waters of hydration from one of the ions (metal) upon formation of the complex, while outer-sphere complexes normally retain most of the waters of hydration. Many metal ions form predominantly outer-sphere complexes with sulphate [monatomic bivalent metal ions (LARSSON, 1964; EIGEN and TAMM, 1962)] while other cationic species form predominantly inner-sphere complexes [iron(III) (ASHHURST and HANCOCK, 1977)]. Spectroscopic and ultrasonic evidence suggests that several complexes are mixtures of inner- and outer-sphere. For example, indium(III)-sulphate is thought to exist as a mixture of 50% inner- and outer-sphere (LARSSON, 1964). These observations regarding relative distributions of inner- and outer-sphere species can account for differences in the thermodynamic properties of these ions or deviations from existing theories.

The present volumetric and heat capacity results for uranyl sulphate complexation are shown along with representative data for several other complexation reactions in Table 12.6. As can be seen the changes in the standard state volumes for most of these reactions are known from the work of Millero, while heat capacities are known for only two species. Differences in the changes in Gibbs free energies, enthalpies and entropies are all consistent with the available data regarding classification as inner- or outer-sphere complexes.

Several theories have been proposed for calculation of the equilibrium constant for ion-pair reactions. The first of these was proposed by BJERRUM (1926). An improved theory and related equation is that due to FUOSS (1958). This latter equation will be discussed in more detail in relation to the present data cited in Table 12.6.

Fuoss theory

Fuoss's theory for ion-pair formation considers cations to be charged spheres with fixed radius a and anions to be point charges. Ion-pair formation is characterized

Table 12.6: Changes in thermodynamic properties for the formation of metal-sulphate complexes by the reaction : $M^{z+}(H_2O)_x + SO_4^{2-} = MSO_4(H_2O)_{x-y}^{2-z} + yH_2O(l)$ at 25°C.

Species	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1}mol^{-1})	$\Delta V°$ (cm^{3}mol^{-1})	$\Delta C_p°$ (J K^{-1}mol^{-1})
Mg^{2+}	−13.2	5.31	61.5	5.8	127
Ca^{2+}	−13.2	6.28	65.3	25	
Mn^{2+}	−12.9	8.61	72.1	7.4	
Co^{2+}	−13.4	6.36	66.4	10.9	
Ni^{2+}	−13.1	6.36	65.7	11.4	
Cu^{2+}	−13.5	7.20	69.5	11.3	
Zn^{2+}	−13.3	5.31	61.5	10.0	
Cd^{2+}	−13.2	9.00	69.5	3.4	
UO_2^{2+}	−18.2	20.2	128.8	−17.3	168
VO^{2+}	−14.1	17.2	105.4		
La^{3+}	−20.0	13.6	113.0	22.8	
Fe^{3+}	−23.7	25.9	163.0		

All thermodynamic properties for the UO_2^{2+}(aq) reaction are from this work. Gibbs free energies, enthalpies, and entropies for Mg^{2+}, Ca^{2+2+} Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}, are from LARSON (1970); Mn^{2+}, Co^{2+}, La^{3+}, and Fe^{3+} were taken from the selections of ASHURST and HANCOCK (1977); and VO^{2+} from BAILEY and LARSON (1971). Changes in volumes were all derived from the results of Millero (MILLERO *et al.*, 1977; CHEN and MILLERO, 1977; MILLERO and MASTERTON, 1974; LO SURDO and MILLERO, 1980). The change in heat capacity for Mg^{2+} was derived from the data of WOOLLEY and HEPLER (1977) in combination with selections for other ions from Chapter 18.

by anions on the surface or inside the volume element of the cation (ROBINSON and STOKES, 1959). The equation derived by Fuoss gives an expression for the equilibrium constant (on a molarity basis) as in (all variables in SI units)

$$K_{A,\ Fuoss} = \frac{4000\pi N_A a^3}{3} \exp\left(\frac{|z_+ z_-|e^2}{4\pi\epsilon_\circ \epsilon a k T}\right) \tag{12.62}$$

where N_A, z_+, z_-, e, $\epsilon_\circ$, ϵ, and k are Avagadro's number, charges on cation and anion, charge of an electron, permitivitty of vacuum, static dielectric constant of solvent, and Boltzmann's constant, respectively. As correctly pointed out by MILLERO (1977) and HEMMES (1972), this equation should be converted to the molality scale for differentiation to avoid temperature dependent concentration units (HEPLER, 1981). Therefore,

$$\ln K_A = \ln K_{A,\ Fuoss} + \ln \rho \tag{12.63}$$

where $\ln K_A$ is now the equilibrium constant with its standard state defined in terms of molality, and ρ is the density of the solvent. LARSON (1970) has shown that predictions using this equation (with a=4.0×10^{-10} m) for bivalent monatomic metal-ion complexation reactions are *extremely* good for changes in free energy, enthalpy, and entropy. HEMMES (1972) and MILLERO (1977) have shown similiar good agreement for some of the associated volume changes of bivalent reactions. The equation fails (in some instances) to mimic the trends with increasing or decreasing radii in the transition metal ions but normally provides reasonable quantitative agreement.

It is of interest here to compare the directly measured volumes and heat capacities for uranyl sulphate complexation with those that can be calculated from the Fuoss equation. The volume change of a reaction is related to the equilibrium constant by

$$\Delta V^\circ = -RT\left(\frac{\partial \ln K}{\partial p}\right)_T \tag{12.64}$$

The Fuoss equation can be differentiated with respect to pressure to give

$$\Delta V^\circ = RT\left[b\left(\frac{\partial \ln \epsilon}{\partial p}\right)_T - \kappa_T\right] \tag{12.65}$$

where

$$b = \frac{|z_+ z_-|e^2}{4\pi\epsilon_\circ \epsilon a k T} = \frac{|z_+ z_-|}{aT} 2.1341 \times 10^{-7} \ \text{m K} \tag{12.66}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \tag{12.67}$$

and all appropriate fundamental constants were taken from TAYLOR *et al.* (1969). At room temperature, $(\partial \ln \epsilon / \partial p)_T$ is positive and the compressibility term is small (HELGESON and KIRKHAM, 1974; KELL, 1967), thus leading to an expected ΔV° for uranyl sulphate complexation of 8.34 $cm^3 mol^{-1}$ based on a from BAILEY and LARSON (1971) calculated to match the experimental Gibbs free energy change. This is in poor agreement with the present $\Delta V^\circ = -17.3$ $cm^3 mol^{-1}$. The Fuoss equation has a lower limit ($a = \infty$) of $-RT\kappa_T$ that equals -1.2 $cm^3 mol^{-1}$, showing that the Fuoss theory cannot predict a ΔV° this negative. MILLERO (1977) has noted that the Fuoss equation underestimates the ΔV° associated with the formation of inner-sphere complexes in complete disagreement with the present results but in agreement with results for the formation of lanthanum (FISHER and DAVIS, 1967) and europium (HALE and SPEDDING, 1972) sulphate complexes. Both of these complexes, however, have a formal ionic charge and thus are expected to have stronger ion-water interactions than these neutral molecules (which should lead to a change in volume less negative), again in conflict with presently observed value for uranyl complexation. Since the ΔV°'s of reaction are directly related to the standard state volumes of the ions, ΔV° values for the formation of cationic-sulphate complexes are plotted versus conventional ionic volumes [based on $\bar{V}^\circ(H^+, aq) \equiv 0$] in Figure 12.6. All conventional ionic volumes for the cationic species were taken from MILLERO (1972) except Eu^{3+}(aq) that was derived using the perchlorate salt (SPEDDING *et al.*, 1975; Chapter 2).

As can be seen in Figure 12.6, UO_2^{2+} is the only species that has a positive conventional volume. The trend displayed by the available data in this Figure would have predicted the observed result for uranyl sulphate formation. This result suggests two things. The first, assuming that the uranyl sulphate complex is predominantly inner sphere, the observations regarding high ΔV°'s for these reactions are partially due to electrostatic changes in the reaction equation (i.e. for europium). Also, it is apparent that the Fuoss equation is completely unsatisfactory for predicting volumetric changes for complex cations (at least of this type) presumably due to differences in the structure of the ion-pair. It appears that the most promising route for explanation of the volumetric changes accompanying these types of reactions will be in the development of theories that predict volumes of the complexed species as

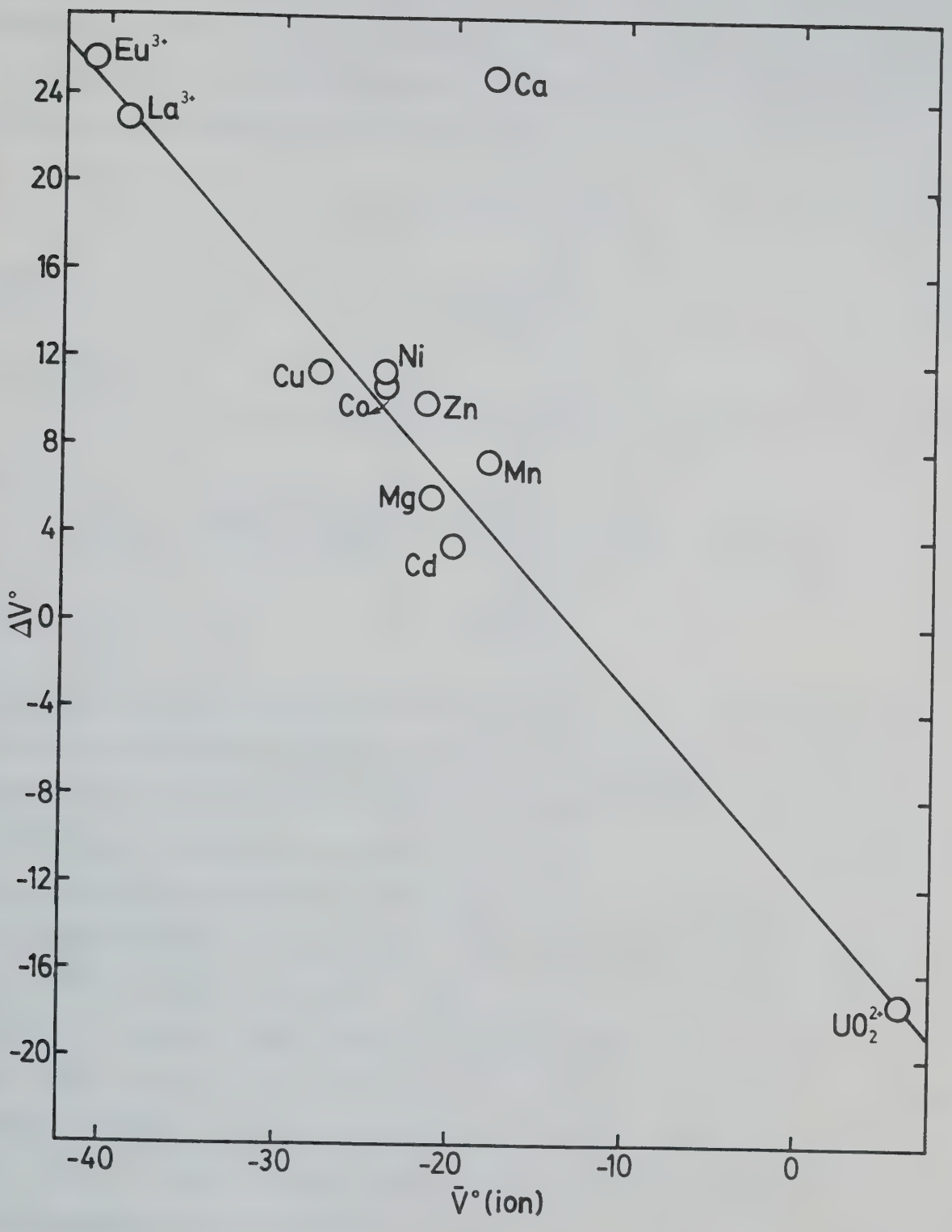

Figure 12.6: Change in volume for sulphate complexation by cationic species versus conventional cationic volumes.

opposed to the reaction properties. It is surprising that the correlation shown in Figure 12.6 does not show the large differences in inner- and outer-sphere complex behaviour as has been shown with other properties (ASHURST and HANCOCK, 1977).

For heat capacity changes associated with ion-pair formation reactions, the Fuoss equation can be differentiated in accord with

$$\Delta H^\circ = RT^2 \left(\frac{\partial \ln K}{\partial T}\right)_p \tag{12.68}$$

and

$$\Delta C_p^\circ = \left(\frac{\partial \Delta H^\circ}{\partial T}\right)_p \tag{12.69}$$

to generate

$$\Delta H_A^\circ = -RTb\left[1 + T\left(\frac{\partial \ln \epsilon}{\partial T}\right)_T\right] - \alpha_p RT^2 \tag{12.70}$$

and

$$\Delta C_{p,A}^\circ = RT^2 \left\{ b\left[\left(\frac{\partial \ln \epsilon}{\partial T}\right)_p^2 - \left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_p\right] - \frac{2\alpha}{T} - \left(\frac{\partial \alpha}{\partial T}\right)_p \right\} \tag{12.71}$$

where

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{12.72}$$

PRUE (1972) derived the first two terms in eq. 12.70 (and an expression for the change in entropy) but failed to recognize the temperature dependency of the molarity based standard state. Values of $(\partial \ln \epsilon/\partial T)_p$ and $(\partial \ln \epsilon/\partial T)_p$ were taken from HELGESON and KIRKHAM (1974) and are positive, and negative, respectively thus leading to a large positive term in the square brackets of eq. 12.71 for most ion-pair formation reactions. The third and fourth terms were calculated using data from KELL (1967) and are both positive and small. Using $a = 3.5\times10^{-10}$m for uranyl sulphate leads to $\Delta C_{p,A}^\circ = 142$ J K^{-1}mol^{-1} that is in excellent agreement with the experimental value 168 J K^{-1}mol^{-1}. It is unclear as to the reason for the models' success in terms of heat capacities and failure for volumes. A similar calculation has lead to the value $\Delta C_{p,A}^\circ = 123$ J K^{-1}mol^{-1} for magnesium sulphate complexation in amazingly good agreement with the experimental value 127 J K^{-1}mol^{-1} from WOOLLEY and HEPLER (1977).

Sulphate is thought to be bonded as a uni-dentate species in inner-sphere complexes (ASHURST and HANCOCK, 1977). As a more general note, species of the type formed by ion-pair formation (such as $MgSO_4$ and UO_2SO_4) have more negative heat

capacities than expected (based on the number of possible molecular motions) much like several ionic species (phosphate, sulphate). The heat capacities of several oxygen containing neutral solutes [see for example CO_2 and SO_2 (BARBERO *et al.*, 1983] have substantially higher heat capacities. Presumably the observed effects in the present sulphate complex come from a combination of the loosely-bound oxygen atoms forming a predominant uni-dentate complex and also from the charge distribution on the species (both of these increasing solute-solvent interactions). These solutes thus are expected to decrease the heat capacity of normal water by the removal of much of the H-bonded structure that gives rise to its anomalously high heat capacity. These same effects would be responsible for the expected negatively divergent volumes and heat capacities for these solutes approaching the critical point of water.

12.5 References

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Chapter 13

Thermodynamics of complexed aqueous uranyl ions II: Experimental apparent molar volumes and heat capacities of aqueous uranyl nitrate and chloride to 55°C. Inadequacies in related thermodynamic data.

13.1 Introduction

As discussed in the previous chapter, thermodynamic data for aqueous uranium(VI) species are required in a variety of applications. $UO_2^{2+}(aq)$ forms strong complexes with many anions including sulphate and carbonate. Aqueous uranyl ion also forms less stable complexes with chloride and nitrate ions (SMITH and MARTELL, 1976).

The present Chapter reports results of measurements (heat capacities and densities) on aqueous solutions containing $UO_2(NO_3)_2$ and UO_2Cl_2 in the presence of dilute acid (HNO_3 and HCl, respectively) from 10 to 55°C. The amounts of complexed and completely dissociated U(VI) must be ascertained for analysis of speciation and subsequent calculation of thermodynamic properties of the complexed ion. The stepwise metal-ligand binding for these systems can be represented by the equation

$$UO_2^{2+}(aq) + nX^-(aq) = UO_2X_n^{2-n}(aq) \qquad (13.1)$$

where $X^-(aq)$ represents either nitrate or chloride. Since the majority of applications involve relatively dilute mixtures of uranyl ion with anions, the most important species are those formed by the first complexation reaction. Since we already have reliable thermodynamic properties for $UO_2^{2+}(aq)$ from Chapter 11, experimental measurements on solutions containing multiple species can potentially be analyzed to provide results for species of the type $UO_2X^-(aq)$ (n=1) that are important for reasons discussed above and in the previous Chapter.

Equilibrium data are required at each of the experimental temperatures in order to calculate amounts of all species present in these solutions. Equilibrium constants are required at each temperature or accurate enthalpies of reaction for evaluation of speciation over this moderate temperature range. Also, because these solutions contain both uncomplexed and complexed aqueous uranyl(VI), accurate enthalpies of reaction are required for calculations of contributions made by chemical relaxation to total measured heat capacities (see the previous Chapter). It became apparent after the presently reported measurements were completed that there are several problems with the existing thermodynamic data for these complex ions. The shortcomings in all of these areas are discussed later in the text. It suffices to state here that the thermodynamic data are insufficient to allow for an accurate calculation of the properties of the complexed species present in these solutions. However, the measurements that lead to apparent molar volumes and heat capacities are correct and can be used along with subsidiary data when they become available.

13.2 Experimental

Water used for all experiments was first passed through an activated charcoal filter and then through a Milli-RO4/Milli-Q reagent grade mixed bed ion exchange and activated carbon system to yield purified water with a resistivity of 18 MΩ cm or greater. Solutions of NaCl (Fisher certified, ACS) were prepared by mass after drying the salt at 110°C until constant weight.

Uranyl nitrate hexahydrate (99%) was obtained from Fisher (certified, ACS) and uranyl chloride hexahydrate from ÆSAR (Johnson Matthey, Canada; 99+%). Concentrated nitric and hydrochloric acids were obtained from Fisher (certified, ACS) and were used without further purification. Both uranyl salts were purified by slow recrystallization from dilute solutions of the corresponding acid.

Stock solutions were prepared by adding the purified salts to solutions approximately 0.05 molal in the corresponding acid. Total uranium in the stock solution was determined gravimetrically using 8-hydroxyquinoline as described by VOGEL (1978). Total anion concentrations in the stock solutions ($2m_2 + m_3$; where m_2 and m_3 are the molalities of the uranyl salt and acid, respectively) were determined by passing

weighed aliquots of the solutions through an ion exchange resin [Rexyn 101(H)] and titrating the eluents with a standard solution of sodium hydroxide. Since all of the solutions investigated here contain complexes of the uranyl cation with the corresponding anion, widely varying amounts of stock solution were passed through the columns. The total amount of anionic concentration in the solution was found to be independent of the amount of stock solution employed, indicating that complete exchange took place. The amounts of excess acid in the stock solutions was obtained by difference. Each stock solution was diluted by mass with standard solutions of the appropriate acid of molality equal to approximately 0.05.

The densities of all solutions were measured relative to water at each of the experimental temperatures ± 0.01 °C with a Sodev 03D vibrating tube densimeter (PICKER *et al.*, 1974), which was calibrated with pure water and a standard solution of NaCl. Densities of the standard NaCl solutions were obtained from the data given by MILLERO (1970). Heat capacities were measured relative to water with a Sodev CP-C Picker type flow microcalorimeter (PICKER *et al.*, 1971). Temperatures were maintained (constant to ± 0.001°C) with separate Sodev CT-L circulating baths and monitored with calibrated thermistors. Daily evaluation of the calorimetric heat loss correction factor (DESNOYERS *et al.*, 1976) by way of measurements on standard solutions of NaCl led to $f = 1.006 \pm 0.001$ at 25°C. This heat loss factor was assumed to be independent of temperature.

13.3 Results

13.3.1 Experimental apparent molar properties

In aqueous solutions containing uranyl ion in the presence of nitrate or chloride, a wide variety of species can exist depending on the pH and relative concentrations of cation and anion. For example, at relatively low pH values and high concentrations of uranyl and either chloride or nitrate, relatively large amounts of complexed species [$UO_2X^+(aq)$] are present (especially in the case of chloride). At higher total concentrations of uranyl ion and ligand, higher complexes may be present (UO_2X_2) (SMITH and MARTELL, 1976). At high pH values (above 2), a variety of monomeric and polymeric uranium-hydroxy species may exist (BAES and MESMER, 1976; LANGMUIR,

1978) and in the presence of chloride and nitrate mixed complexes may also be present depending on the relative concentrations of all species.

In an attempt to reduce complicating factors, the measurements described here were all performed on solutions containing sufficient acid to enable neglect of all of the hydrolyzed species. Also because of the complications associated with calculating data for species present in very small amounts (as is the case here for all of these solutions upon extrapolation to infinite dilution), only small excesses of the corresponding anions were used to minimize formation of higher complexes.

Values for the density and specific heat capacity of pure water at each of the experimental temperatures were taken from Chapter 4 (Table 4.2, KELL, 1967; 1972). The relative densities $(d - d_1^\circ)$ and heat capacity ratios $(c_p d / c_{p,1}^\circ d_1^\circ - 1)$ for the aqueous solutions containing $UO_2(NO_3)_2 + HNO_3$ and $UO_2Cl_2 + HCl$ are listed in Table 13.1 at each of the experimental temperatures. The "experimental" apparent molar property ${}^\phi Y^{exptl}$ of a solution is defined by

$$ {}^\phi Y^{exptl} = \frac{Y_{soln} - 55.509 Y_1^\circ}{m_2 + m_3} \tag{13.2} $$

where Y_{soln} is the extensive property (volume or heat capacity) of a solution that contains 1 kilogram of solvent (water), Y_1° is the molar volume or heat capacity of pure solvent (water), and m_2 and m_3 are the stoichiometric molalities of the uranyl salt and the appropriate acid. Experimental apparent molar volumes and heat capacities were calculated from the results listed in Table 13.1 by the equations

$$ {}^\phi V^{exptl} = \frac{\frac{1 + m_2 M_2 + m_3 M_3}{d} - \frac{1}{d_1^\circ}}{m_2 + m_3} \tag{13.3} $$

and

$$ {}^\phi C_p^{exptl} = \frac{c_p (1 + m_2 M_2 + m_3 M_3) - c_{p,1}^\circ}{m_2 + m_3} \tag{13.4} $$

where M represents the solute molar mass, c_p and d are the specific heat capacity and density of the solution, and $c_{p,1}^\circ$ and d_1° are the specific heat capacity and density of pure water. All of these experimental apparent molar volumes and heat capacities are listed in Table 13.1.

Many equilibrium studies have led to reports of complexation constants for uranyl ion with chloride or nitrate. The complexation reaction that is of most interest in

Table 13.1: Compositions of solutions and experimental apparent molar volumes and heat capacities for $UO_2(NO_3)_2$ + HNO_3 and UO_2Cl_2 + HCl mixtures.

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	${}^\phi V^{exptl}$ (cm^{3}mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	${}^\phi C_p^{exptl}$ (J K^{-1}mol^{-1})
		UO_2Cl_2 + HCl			
		10°C			
0.8065	0.2251	23.0770	41.232	−6.151	−89.59
0.4993	0.1583	14.4491	41.826	−4.296	−107.99
0.4191	0.14092	12.2036	41.324	−3.775	−117.90
0.3676	0.1297	10.7493	40.920	−3.379	−121.15
0.2845	0.1117	8.3801	40.186	−2.765	−130.76
0.2159	0.09678	6.4079	39.225	−2.176	−132.90
0.1618	0.085013	4.8317	38.336	−1.725	−137.20
0.06548	0.064102	2.0343	32.623	−0.886	−153.11
0.05529	0.06189	1.7319	31.747	−0.788	−151.98
0.05195	0.061163	1.6338	31.307	−0.759	−153.13
		25°C			
0.8065	0.2251	22.6294	44.542	−5.215	−36.85
0.4993	0.1583	14.3257	43.107	−3.677	−62.27
0.4191	0.14092	12.1013	42.580	−3.208	−69.31
0.3676	0.1297	10.6556	42.245	−2.884	−73.07
0.2845	0.1117	8.3135	41.350	−2.351	−81.50
0.2159	0.09678	6.3578	40.341	−1.879	−87.97
0.1618	0.085013	4.8016	39.117	−1.499	−94.99
0.06548	0.064102	2.0181	33.539	−0.787	−117.01
0.05529	0.06189	1.7244	32.078	−0.705	−120.28
0.05195	0.061163	1.6206	32.168	−0.671	−116.45
		40°C			
0.8065	0.2251	22.4898	45.011	−4.525	−6.409
0.4993	0.1583	14.2446	43.479	−3.220	−31.56
0.4191	0.14092	12.0347	42.919	−2.815	−38.59
0.3676	0.1297	10.5989	42.5450	−2.552	−44.04
0.2845	0.1117	8.2693	41.645	−2.091	−52.95

Table 13.1: (continued).

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	ϕV^{exptl} (cm^{3}mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	ϕC_p^{exptl} (J K^{-1}mol^{-1})
0.2159	0.09678	6.3246	40.614	−1.672	−59.43
0.1618	0.085013	4.7778	39.328	−1.341	−67.74
0.06548	0.064102	2.0087	33.673	−0.727	−97.29
0.05529	0.06189	1.7126	32.529	−0.655	−101.35
0.05195	0.061163	1.6157	32.065	−0.627	−101.33
		55°C			
0.8065	0.2251	22.4683	44.235	−3.928	14.79
0.4993	0.1583	14.2384	42.537	−2.829	−10.75
0.4191	0.14092	12.0286	41.979	−2.491	−18.59
0.3676	0.1297	10.6019	41.440	−2.260	−24.42
0.2845	0.1117	8.2761	40.430	−1.862	−34.30
0.2159	0.09678	6.3271	39.500	−1.475	−38.21
0.1618	0.085013	4.7830	38.119	−1.236	−55.73
0.06548	0.064102	2.0135	32.489	−0.686	−89.77
0.05529	0.06189	1.7194	31.181	−0.628	−97.87
0.05195	0.061163	1.6178	31.138	−0.604	−97.26
		$UO_2(NO_3)_2$ + HNO_3			
		10°C			
0.8638	0.01795	26.4144	69.342	−5.723	0.051
0.5703	0.02885	17.8127	68.520	−4.245	−24.03
0.4324	0.03395	13.6833	67.261	−3.445	−39.52
0.3122	0.03841	10.0422	64.740	−2.666	−56.85
0.2473	0.04081	8.0425	62.839	−2.206	−65.60
0.1495	0.04443	4.9796	58.519	−1.483	−80.95
0.09322	0.04652	3.1794	54.531	−1.035	−86.24
0.05754	0.04783	2.0342	49.669	−0.741	−89.90
0.04427	0.04833	1.6095	46.664	−0.630	−92.48
		25°C			
0.8638	0.01795	25.9664	73.156	−5.076	47.13
0.6839	0.02464	20.8767	72.169	−4.286	33.32

Table 13.1: (continued).

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	ϕV^{exptl} (cm^{3}mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	ϕC_p^{exptl} (J K^{-1}mol^{-1})
0.5703	0.02885	17.5850	71.382	−3.742	23.54
0.4382	0.03374	13.6863	70.1155	−3.062	10.23
0.3122	0.03841	9.8955	68.117	−2.338	−3.344
0.2473	0.04081	7.9204	66.324	−1.938	−11.96
0.1495	0.04443	4.8913	62.429	−1.291	−23.25
0.09322	0.04652	3.1269	57.772	−0.907	−34.54
0.05754	0.04783	2.0014	52.378	−0.649	−42.42
0.04427	0.04833	1.5802	49.475	−0.554	−46.62
0.02121	0.04918	0.8488	41.579	-0.385_4	−57.67
			40°C		
0.8638	0.01795	25.6810	75.067	−4.683	73.22
0.6839	0.02464	20.6830	73.675	−3.966	57.900
0.5703	0.02885	17.3897	73.386	−3.466	50.40
0.4382	0.03374	13.5501	71.825	−2.844	35.87
0.3122	0.03841	9.7923	69.938	−2.184	21.63
0.2473	0.04081	7.8341	68.243	−1.813	13.06
0.1495	0.04443	4.8431	63.973	−1.224	−3.410
0.09322	0.04652	3.0956	59.201	−0.859	−15.227
0.05754	0.04783	1.9814	53.613	−0.617	−25.29
0.04427	0.04833	1.5625	50.810	−0.520	−26.68
			55°C		
0.8638	0.01795	25.5429	75.260	−4.390	86.97
0.5703	0.02885	17.3113	73.324	−3.270	62.59
0.4382	0.03374	13.4819	71.886	−2.677	49.60
0.4324	0.03395	13.3067	71.926	−2.686	46.117
0.3122	0.03841	9.7491	69.824	−2.071	33.14
0.2473	0.04081	7.7968	68.215	−1.722	24.76
0.1495	0.04443	4.8217	63.859	−1.164	7.623
0.09322	0.04652	3.0771	59.464	−0.850	−13.04
0.05754	0.04783	1.9709	53.731	−0.600	−19.50

these solutions can be represented in terms of the fractional extent of reaction (α) by

$$\begin{array}{ccccc} UO_2^{2+}(aq) & + & X^-(aq) & = & UO_2X^+(aq) \\ (1-\alpha)m_{2,i} & & [(2-\alpha)m_{2,i}+m_3] & & \alpha m_{2,i} \end{array} \qquad (13.5)$$

where X=Cl or NO_3. Each of the solutions under present investigation thus contained three combinations of ions that can be represented by the following pairs of ions: $[UO_2^{2+}(aq) + 2X^-(aq)](m_2)$, $[H^+(aq) + X^-(aq)](m_3)$, and $[UO_2X^+(aq) + X^-(aq)](m_4)$.

The experimental apparent molar properties of the solutions can be separated into terms representing each of the species present in the solution by using Young's rule[1] (YOUNG and SMITH, 1954) :

$$^{\phi}Y^{exptl} = \frac{m_2}{m_2+m_3+m_4}{}^{\phi}Y_2 + \frac{m_3}{m_2+m_3+m_4}{}^{\phi}Y_3 + \frac{m_4}{m_2+m_3+m_4}{}^{\phi}Y_4 + \delta \qquad (13.6)$$

Here $^{\phi}Y_2$, $^{\phi}Y_3$, and $^{\phi}Y_4$ all apply at the *total* ionic strength of the solution, and δ is an excess mixing term arising from non-ideal ion interactions. The δ term was ignored in subsequent calculations because of inabilities to apply any statistical significance to the term (due to the exceedingly small amounts of the desired solute present in all of these solutions).

As discussed in detail in several previous Chapters, measured heat capacities of solutions that contain an associating (as is the case here) or dissociating solute contain contributions from the nature and amounts of the chemical species present, and also contributions from "chemical relaxation". Calculations of the magnitude of these relaxation contributions require the same data that are needed to assess the equilibrium amounts of each species present in these solutions. The discussion on relaxation corrections will thus be deferred until an analysis of the presently available thermodynamic data for uranyl-complex aqueous ions is completed.

13.3.2 Thermodynamic data for $UO_2Cl^+(aq)$ and $UO_2NO_3^+(aq)$

Equilibrium constants

As mentioned previously, the available thermodynamic data for the aqueous com-

[1]Strictly speaking the original "experimental" properties that apply in Young's rule are those defined in terms of each of the equilibrium molalities m_2, m_3, and m_4. However, since $m_{2,i} + m_3 = m_2 + m_3 + m_4$, the resultant properties are identical.

plexes of nitrate and chloride with uranyl ion are plentiful but inconsistent. The compilations by SILLÉN and MARTELL (1964, 1971), SMITH and MARTELL (1976), HÖGFELDT (1982), and FUGER *et al.* (in prep.) cite the majority of equilibrium data for both nitrate and chloride complexation by uranyl ion. Most of these data along with some additonal measurements are listed in Tables 13.2 and 13.3 for the nitrate and chloride complexes, respectively (some obviously incorrect results are not included in these tables).

The standard state thermodynamic equilibrium constant (infinite dilution) can be represented by

$$K = Q\gamma_r \tag{13.7}$$

where $\gamma_r = (\gamma_{UO_2X^+}/\gamma_{UO_2^{2+}}\gamma_{X^-})$, and Q is the apparent (ignoring activity coefficients) equilibrium constant or equilibrium quotient of the reaction at some finite ionic strength. The extended Debye-Hückel equation

$$\ln \gamma_i = \frac{z_i^2 A_\gamma I^{1/2}}{1 + \text{å} B_\gamma I^{1/2}} \tag{13.8}$$

can be used to represent the activity coefficients of all of the appropriate species, where A_γ and B_γ are constants, and å is an ion-size parameter. WALLACE (1967) found that values of å = 7 fit his data for uranyl sulphate complexation best. It is thus expected that for uranyl nitrate and chloride complexation, best values will probably be near or lower than this value, respectively, based on ionic radii considerations. Equilibrium constants obtained at finite ionic strengths can be extrapolated to infinite dilution by combining the above equations to obtain

$$\ln Q = \ln K - \frac{4A_\gamma I^{1/2}}{1 + \text{å} B_\gamma I^{1/2}} + BI \tag{13.9}$$

where B accounts for any concentration dependence in $\ln Q$.

For nitrate complexation, the results of OHASHI and MOROZUMI (1967) suggest that the limiting value of $\ln K$ is about one. The data from MARCANTONATOS *et al.* (1980) suggest a *much* lower value. Some of the inconsistencies in the available data are illustrated by noting that the value determined by LAHR and KNOCH (1970) is approximately 2 units in $\ln K$ different from the results of BETTS and MICHELS (1949). As also can be seen from the available data, no study presents a comprehensive investigation of the equilibrium constants over wide ranges of ionic

Table 13.2: Thermodynamic data for the reaction $UO_2^{2+}(aq) + NO_3^-(aq) = UO_2NO_3^+(aq)$.

t (°C)	I	Q	Method*	Reference
20	1M $NaClO_4$	0.50	emf	AHRLAND (1951)
25	5.38M (Na, H)(ClO_4, NO_3)	0.21	spec	BETTS and MICHELS (1949)
	7.0M (Na, H)(ClO_4, NO_3)	0.27		
10	2M $NaClO_4$	0.30	dist	DAY and POWERS (1954)
25		0.24		
40		0.17		
32	1M $NaClO_4$	0.04	exch	BANERJEA and TRIPATHI (1961)
25	0.54M Na(NO_3, ClO_4)	0.37	emf	OHASHI and MOROZUMI (1967a)
	0.82M Na(NO_3, ClO_4)	0.20		
	1.06M Na(NO_3, ClO_4)	0.19		
20	8M $HClO_4$	2.94	dist	LAHR and KNOCK (1970)
22	0M ($NaClO_4$)	0.25		MARCANTONATOS *et al.* (1980)
	0.23			
	2M ($NaClO_4$)	0.29		
25	0.71M $HClO_4$	0.63	dist	PUSHLENKOV *et al.* (1960)
23	6.25M Na(ClO_4, NO_3)	0.15	spec	BROOKER *et al.* (1980)

Abbreviations used are:
emf: potentiometric
spec: spectroscopic
dist: distribution (water/organic phase)
exch: ion exchange
fp: freezing point

strengths. Our selected "best" value for $\ln K$ and B come from fitting eq. 13.9 to the results that are considered most reliable (AHRLAND, 1951; BETTS and MICHELS, 1949; OHASHI and MOROZUMI, 1967; DAY and POWERS, 1944) and are summarized by

$$\ln Q = 0.23 - \frac{4.7253 I^{1/2}}{1 + 2.304 I^{1/2}} + 0.0145 I \qquad (13.10)$$

where all quantities are applicable to solutions with concentrations in molarity. The estimated error in $\ln K$ from the least squares fits was $\pm$ 0.21, corresponding to an equilibrium constant of 1.26 ± 0.3.

There are relatively large discrepancies in equilibrium constants determined by different workers for uranyl chloride complexation. Most of the available results are summarized in Table 13.2. For example, at ionic strengths near one molar, the spread in equilibrium constants is over two units in the natural logarithim of Q (plus the Debye-Hückel term). The "best" results are probably those of NELSON and KRAUS (1951), AHRLAND (1951), BALE *et al.* (1957), and DAVIES and MONK (1957), although several other studies such as those of AWASTHI and SUNDARESAN (1981) and BUNUS (1972) deserve consideration. However, many of these studies show several problems. For example, in the report from DAVIES and MONK (1957) there are several inconsistencies in the tabulated results. LEMIRE and TREMAINE (1980) report that their analysis of these results lead to a significantly higher association constant at infinite dilution ($\log K > 1$ rather than the suggested $\log K = 0.22$). The results presented by AWASTHI and SUNDARESAN (1981) as a function of temperature were used incorrectly in calculations of the enthalpy changes associated with the complexation reaction. Their reported fits to equilibrium data also do not correspond to their calculated enthalpies whether done correctly (considering changes in molarities with temperature) or incorrectly (not considering these changes). With consideration of these and other factors, it is difficult to suggest a "best" expression for the equilibrium constants for uranyl complexation with chloride ion. Of the studies that clearly have studied ionic strength effects, the results of BALE *et al.* (1957), BUNUS (1972), and AWASTHI and SUNDARESAN (1981) were all used in a variety of calculations that are described later.

Table 13.3: Thermodynamic data for the reaction $UO_2^{2+}(aq) + Cl^-(aq) = UO_2Cl^+(aq)$.

t (°C)	I	Q	Method*	Reference
20	1M $NaClO_4$	0.80	emf	AHRLAND (1951)
		0.50	spec	AHRLAND (1951)
10	2M $NaClO_4$	0.58	dist	DAY and POWERS (1954)
25		0.88		
40		1.14		
25	1M $NaClO_4$	0.35	spec	RUSH and JOHNSON (1963)
		0.52		
25	0	2.40	spec	NELSON and KRAUS (1951)
25	0	0.80	exch	KRAUS *et al.* (1955)
25	0	1.61	spec	DAVIES and MONK (1957)
25	0	1.67	spec	BALE *et al.* (1957)
32	1M $NaClO_4$	2.00	exch	BANERJEA and TRIPATHI (1961)
25	0.54M (K,Na)(NO_3,ClO_4)	2.42	emf	OHASHI and MOROZUMI (1967a)
	0.82M (K,Na)(NO_3,ClO_4)	1.40		
	1.06M (K,Na)(NO_3,ClO_4)	0.89		
15	0 KNO_3	19.6	emf	OHASHI and MOROZUMI (1967b)
25	0	15.4		
35	0	13.0		
-3	sat KNO_3	1.8	fp	FOUCHERRE (1962)
20	8M $HClO_4$	0.82	dist	LAHR and KNOCK (1970)
25	0	1.70	spec	AWASTHI and
35	0	1.86		SUNDARESAN (1981)
45	0	2.04		
25	0.6	1.005	exch	BUNUS
	2.0	1.06		
	4.0	2.01		
25	1.23M $NaClO_4$	43.9	spec	HEFLEY and AMIS (1960)
50	0.03M	1.87	emf	NIKOLAEVA (1977)
70	0.03M	1.96		
90	0.03M	2.23		
100	0.03M	2.40		
125	0.03M	2.75		
150	0.03M	3.25		

See Table 13.2 for list of abbreviations.

Enthalpies

Only two studies have been reported with results that lead to the enthalpy of uranyl nitrate complexation. MARCANTONATOS *et al.* (1980) and DAY and POWERS (1954) have both reported equilibrium constants obtained as a function of temperature that lead to enthalpies {corrected to include effects of temperature on molarity [HEPLER (1981)]} of reaction and thence $\Delta H°(I = 0) = 3.1$ and $\Delta H(I = 2) = -14$ kJ mol^{-1}. The former value appears to be more reliable. DAY and POWERS (1954) also suggest that the observed temperature effect on their determined equilibrium constants may be completely due to ionic strength effects and they recommend against using their reported value.

There are several results that can be used to derive the enthalpy changes associated with uranyl chloride complexation. For example, temperature dependent studies have been reported by AWASTHI and SUNDARESAN (1981), OHASHI and MOROZUMI (1967b), DAY and POWERS (1954), and NIKOLAEVA (1977). AWASTHI and SUNDARESAN (1981) have also reported a calorimetrically determined enthalpy change associated with uranyl chloride complexation at an ionic strength of 4.9M. The highly endothermic enthalpy reported by OHASHI and MOROZUMI (1967b) is completely inconsistent with all of the other results. The value derived by NIKOLAEVA (1977) is based on equilibrium measurements from 50 to 150°C at an ionic strength of 0.03 molar. He has combined the equilibrium constant at 25°C and 1.238 molar from HEFLEY and AMIS (1960) with his results for calculation of the enthalpy change. Attempts to use other (probably better) results at 25°C and an ionic strength of 0.03 molar along with the higher temperature results proved unsatisfactory. The expected large heat capacity change of these reactions make differentiation of equilibrium constants prone to large errors. The large spread in these results also makes it difficult to select "best" values. Combinations of several different studies were used in calculations described in the following section, all that proved unsatisfactory.

Relaxation corrections for nitrate and chloride salts

It appears that discrepancies in the necessary thermodynamic data prevent a rigorous analysis of speciation in solutions containing uranyl chloride and nitrate, even at 25°C. Nevertheless, the method of assessing contributions due to chemical relaxation (used in calculations that follow later) is presented here so that it may be used when appropriate data become available.

The reaction of interest here is the ion-pair formation reaction of uranyl with either nitrate or chloride ion designated by X:

$$\begin{array}{ccccc} UO_2^{2+}(aq) & + & X^-(aq) & = & UO_2X^+(aq) \\ (1-\alpha)m_{2,i} & & [(2-\alpha)m_{2,i}+m_3] & & \alpha m_{2,i} \end{array} \tag{13.5}$$

It has been shown (WOOLLEY and HEPLER, 1977; Chapters 12,16) that the contribution of chemical relaxation to "exptl" apparent molar heat capacities of solutes containing an associating (or dissociating) solute in the presence of an inert solute (such as the case here) is given by

$${}^{\phi}C_{p,\Sigma}^{rel} = \frac{m_2}{m_2+m_3}\Delta H\left(\frac{\partial\alpha}{\partial T}\right)_{p,m_2} \tag{13.11}$$

where ΔH represents the change in enthalpy of the association reaction at the total ionic strength of the solution, and m_2 and m_3 are the stoichiometric molalities of UO_2X_2 and HX.

An analysis of the appropriate equations for this system begins by differentiating the equilibrium constant expression (eq. 4) in terms of concentrations of species (using Q instead of K and γ's) that leads to the desired expression:

$$\left(\frac{\partial\alpha}{\partial T}\right)_{p,m_2}\left\{m_2Q(2\alpha-3)-m_2m_3Q-1+2m_2^2\left(\frac{\partial Q}{\partial I}\right)_{T,p}\times \left[m_3Q-m_3-(1-3\alpha+\alpha^2)\right]\right\} = m_2\left(\frac{\partial Q}{\partial T}\right)_{p,I}\left[m_3Q-m_3-(1-3\alpha+\alpha^2)\right] \tag{13.12}$$

Here

$$\left(\frac{\partial Q}{\partial T}\right)_{p,I} = \frac{Q\Delta H}{RT^2} \tag{13.13}$$

$$\left(\frac{\partial Q}{\partial T}\right)_{p} = \left(\frac{\partial Q}{\partial T}\right)_{p,I} - 2m_2\left(\frac{\partial\alpha}{\partial T}\right)_{p}\left(\frac{\partial Q}{\partial I}\right)_{T,p} \tag{13.14}$$

Equation 13.14 results from the dependence of the apparent equilibrium constant on both temperature and ionic strength. Evaluation of $(\partial Q/\partial I)_{T,p}$ from expressions of the type given by Debye-Hückel theory were illustrated in the preceding Chapter.

13.3.3 Calculations

Calculations of speciation and relaxation for all of the solutions of present interest were carried out using combinations of the data discussed above with emphasis on the selected "best" values. Equilibrium constants at 10, 40, and 55°C were derived from the selected enthalpy of MARCANTONATOS *et al.* (1980) for nitrate complexation and various selections for uranyl chloride complexation. These calculations have led to values for α and hence equilibrium concentrations of all species present in the solutions.

These data were used in calculations of the apparent molar properties of individual components from the experimental apparent molar properties by way of Young's rule (eq. 13.6) and the following information. The ionic strength dependences of the apparent molar properties for the species (UO_2X^+, X^-) were assumed to be adequately represented by extended Debye-Hückel equations of the type

$$^{\phi}Y_2 = \bar{Y}_2^{\circ} + \frac{3}{2}\omega A_Y \left(\frac{1}{\Lambda} - \frac{\sigma}{3}\right) I^{1/2} + B_Y I + C_Y I^{3/2} \tag{13.15}$$

where

$$I = \omega m = \frac{1}{2}\sum m_i z_i^2 \tag{13.16}$$

$$\Lambda = 1 + I^{1/2} \tag{13.17}$$

$$\sigma = \frac{3\left(\Lambda - \frac{1}{\Lambda} - 2\ln\Lambda\right)}{I^{3/2}} \tag{13.18}$$

Values for the Debye-Hückel limiting slopes (A_Y) were taken from ANANTHASWAMY and ATKINSON (1984) and are listed in Chapter 4, Table 4.2.

Apparent molar volumes and heat capacities are required for all species that are present in these solutions. Apparent molar volumes for the species (UO_2^{2+}, $2X^-$) and for the excess acid HX were calculated as follows. Results for: $UO_2(ClO_4)_2$ and $HClO_4$ from 10 to 55°C were taken from Chapters 4 and 11; hydrochloric acid volumes were taken from ALLRED and WOOLLEY (1981) from 10 to 40°C and from HERRINGTON *et al.* (1985) at 55°C, heat capacities at 25°C from DESNOYERS *et*

al. (1976), and at 10, 40, and 55°C from TREMAINE *et al.* (1986); all properties for nitric acid were taken from Chapter 4. Estimates of the apparent molar properties of (UO_2^{2+}, $2X^-$) were calculated from the scheme

$$^{\phi}Y(UO_2^{2+},\ 2X^-) = {}^{\phi}Y(2UO_2^{2+},\ 2ClO_4^-) - 2^{\phi}Y(H^+,\ ClO_4^-) + 2^{\phi}Y(H^+,\ X^-) \quad (13.19)$$

Expressions given by eqs. 13.15-13.18 were fitted to the experimental apparent molar properties using Young's rule (eq. 13.6). Plots of the calculated apparent molar volumes of the species (UO_2X^+, X^-) minus the appropriate Debye-Hückel term showed a highly uncharacteristic curvature in the dilute region, which suggests shortcomings in equilibrium constants and their ionic strength dependences. It was apparent from several trials using various combinations of the data cited above that discrepancies in the existing data at room temperature prevents an unambiguous determination of the apparent molar properties of the complexed species (UO_2X^+, X^-). Analyses of apparent molar heat capacities were not so much affected by the choices of equilibrium constants, but the non-characteristic curvature in plots of the derived apparent molar heat capacities minus the Debye-Hückel limiting law at very low ionic strengths also makes these calculations suspect. In all of these calculations, the formation of complexes with more than one anion was ignored (more experimental data are required to treat the results if multiple equilibria are responsible for such uncharacteristic behaviour).

Expressions of the type given by eqs. 13.15 to 13.18 were also fitted to the results by assuming that no complexation occurred. Results of these fits strongly support the previous suggestion that there is significant complexation in these solutions. In both cases the limiting standard state properties that can be calculated for uranyl ion are substantially different than such calculations based on data for uranyl perchlorate as in Chapter 11.

13.4 Discussion

Several authors have reported volumes and heat capacities of aqueous solutions containing uranyl chloride and nitrate, as already discussed in Chapter 12. MANZUROLA and APELBLAT (1985) have made densimetric measurements on aqueous solutions

containing $UO_2(NO_3)_2$, UO_2Cl_2, and UO_2SO_4 to very low ionic strengths. They have treated their results by assuming negligible hydrolysis and complete dissociation of each salt. These assumptions are incorrect as indicated by the preceding discussion and also by their own calculations of the limiting standard state volumes for uranyl ion. STANKOV *et al.* (1973) have also reported apparent molar volumes for the nitrate and chloride salts from which they have identified stages in the stepwise association reactions. Apparent molar volumes are extremely sensitive to these types of ion pair formation reactions and provide useful information regarding the state of the aqueous ions. Future results that satisfy calculations of apparent molar volumes will likely be the most reliable.

13.4.1 Suggested experiments

The present heat capacities and volumes can only be used properly when better equilibrium data become available. The heat capacities that can be derived at room temperature (once more accurate equilibrium data are known) can be used to refine the presently available enthalpies, or to represent the temperature dependence of a calorimetrically determined enthalpy of reaction. There is no special requirement to do any experiments at temperatures other than room temperature, although these data would also be of some use.

It is apparent that room temperature equilibrium constants are required for an analysis of complexation of uranyl halides and nitrate, all experiments being carried out with sodium perchlorate or some other non-complexing supporting electrolyte such as sodium trifluoromethanesulphonate. It appears that the "best" methods for the determination of the equilibrium constants for these reactions are potentiometric or spectroscopic. An extensive study of equilbrium constants by both methods [much like the study of AHRLAND (1951)] over widely varying ionic strengths with more sensitive and modern equipment would likely unambiguously define these weak ion-pair formation constants for nitrate and chloride. Accurate calorimetric measurements leading to enthalpies of reaction as a function of ionic strength are also required. Enthalpy measurements of the type recently reported by GRENTHE *et al.* (1986) for uranyl complexation with carbonate should be useful for methodology. A completely rigorous determination of relaxation effects for measured heat

capacities of solutions requires that enthalpies of dilution be known for each species present. Such data are already available for uranyl nitrate complexation (LANGE and MIEDERER, 1957).

13.5 References

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Chapter 14

Thermodynamics of aqueous EDTA systems : Apparent and partial molar heat capacities and volumes of aqueous strontium and barium EDTA[1]

14.1 Introduction

Aqueous solutions of ethylenediaminetetraacetic acid (EDTA) are used as sequestering agents in a number of industrial applications that include cleaning various kinds of boilers, softening boiler and process water, treating oil wells to remove scales and certain minerals, and decontaminating nuclear reactor systems. In all of these applications the principal focus is on complexation of divalent (such as investigated here) or trivalent ions. The complexation equilibria of most metal ions of interest have already been investigated at or near 25°C, but many of the applications involve temperatures considerably higher than 25°C for which there are no equilibrium data. The "missing" equilibrium constants for high temperature solutions can be calculated from a combination of already known stability constants and enthalpies of complexation at 25°C with the heat capacities that form the main part of this investigation and also other investigations (Chapter 15, HOVEY and TREMAINE, 1985) of other metal ion-EDTA systems; results of such equilibrium calculations are presented later in this chapter.

One specific reason for investigating complexes of EDTA with strontium and barium ions is that $SrSO_4$ and/or $BaSO_4$ are sometimes deposited as scales in conventional and heavy oil equipment when high sulfate brines are produced along with the desired oil. A more general reason for this extension of our earlier work(1) is to provide an extended data base for improved correlation or predictive schemes for

[1] A version of this chapter has been published. Hovey, J.K.; Hepler, L.G.; Tremaine, P.R. *Journal of Solution Chemistry*, **15**, 977-987 (1986).

the thermodynamics of complexation of metal ions by EDTA.

The experimental work described in this Chapter has led to heat capacities and densities of metal ion/EDTA aqueous solutions. Results of these measurements are reported in the form of apparent and partial molar heat capacities and volumes, which are directly useful in the thermodynamic calculations mentioned in preceding paragraphs.

14.2 Experimental

Water used for all solutions was distilled, passed through a Milli-Q reagent grade mixed bed ion exchange and activated carbon system to yield product water with a final resistance of 18 MΩ cm or greater. Standard solutions of NaCl were prepared by mass after drying the salt (Fisher certified, ACS) at 110°C for several hours.

$Na_2BaEDTA$ (ICN Pharmaceuticals) was recrystallized twice by a method derived from VOGEL (1978). A saturated solution of the solute in water was formed by gentle heating, to which 95% ethanol was added dropwise with vigorous stirring. At the first sign of a permanent precipitate, a volume of ethanol equal to the initial volume was added dropwise over several hours. The solution was filtered and the filtrate was washed with ethanol. This procedure was then repeated. $Na_2SrEDTA$ was prepared by the reaction of a slightly alkaline solution of Na_2H_2EDTA (Fisher certified) with a small excess of $SrCl_2 \cdot 6H_2O$ (Fisher certified). The crystals of $Na_2SrEDTA{\cdot}xH_2O$ were collected after addition of ethanol and were then recrystallized twice in the same manner as for the barium salt. Both salts were dried at 60°C for five days. Stock solutions of the salts were prepared by mass from these dried (but still hydrated) salts. Total water contents of the dried salts were obtained from the mass loss on complete dehydration of the salts at 150°C under vacuum; this information was then used in calculating molalities of the various solutions.

Heat capacities of all solutions were measured at 25.00 ± 0.05°C with a Picker flow microcalorimeter (PICKER *et al.*, 1971). The specific heat capacity of water was taken from KELL (1972) and had the value 4.1793 J $K^{-1}g^{-1}$. Small corrections to the raw heat capacity data were made to allow for heat losses in the calorimeter, as described by DESNOYERS *et al.* (1976), and in Chapter 2. Values of the heat leak

correction factor f, which ranged between 1.003 and 1.007, were determined daily from measurements on standard NaCl solutions.

Densities of all solutions were measured relative to water at 25.00 ± 0.01°C with a Sodev 03D vibrating tube densimeter (PICKER *et al.*, 1974), which was calibrated with water and standard NaCl solutions. The density of water was taken from KELL (1967) and had the value 0.997047 g cm^{-3}. Densities of the standard NaCl solutions were taken from the results of PICKER *et al.* (1974).

Temperature control for the densimeter and calorimeter was achieved with separate Sodev CT-L circulating baths (constant to ± 0.001 °C). Temperatures of the baths were monitored with thermistors that had been calibrated against a Hewlett-Packard 2804A quartz crystal thermometer.

14.3 Results

Experimental results from the Picker calorimeter and densimeter are conveniently expressed (Table 14.1) in terms of $\left(\frac{c_p d}{c^\circ_{p,1} d^\circ_1} - 1\right)$ and $(d - d^\circ_1)$ in which c_p and $c^\circ_{p,1}$ are the specific heats of solution and of pure water and d and d°_1 are the densities of solution and of pure water. For our thermodynamic calculations it is most useful to begin by expressing these experimental results in the form of apparent molar properties ($^\phi C_p$ and $^\phi V$) that are defined generally by

$$^\phi Y = \frac{Y_{sol} - n_1 Y^\circ_1}{n_2} \tag{14.1}$$

in which Y_{sol} is the extensive property (heat capacity or volume) of a specified quantity of solution, Y°_1 is the property (heat capacity or volume) of one mole of pure water, and n_1 and n_2 are the amounts (moles) of water and of solute in the specified quantity of solution. These $^\phi C_p$ and $^\phi V$ results are also listed in Table 14.1.

Stability constants from MARTELL and SMITH (1974) were used in calculating that less than 0.1% of the $MEDTA^{2-}(aq)$ complexes were dissociated in the solutions. It is therefore appropriate to regard these solutions as containing electrolytes of type $2Na^+/MEDTA^{2-}(aq)$.

Apparent molar properties can be represented accurately to moderate concentra-

Table 14.1: Results of calorimetric and densimetric measurements at 25.0°C.

m (mol kg^{-1})	$10^3(d - d_1^\circ)$ (g cm^{-3})	$^\phi V$ (cm^3 mol^{-1})	$\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	$^\phi C_p$ (J K^{-1}mol^{-1})
		Na_2SrEDTA		
0.12277	31.057	163.49	−0.01291	231.2
0.095541	24.336	162.86	−0.01029	219.3
0.084508	21.589	162.56	−0.009253	211.5
0.064003	16.443	161.96	−0.007144	201.5
0.049314	12.723	161.47	−0.005608	191.7
0.031407	8.139	161.06	−0.003668	178.5
0.017775	4.618	160.97	−0.002116	169.5
		Na_2BaEDTA		
0.14808	44.005	166.64	−0.01369	296.8
0.11404	34.144	166.07	−0.01088	284.1
0.096788	29.072	165.95	−0.009443	275.4
0.08126	24.520	165.33	−0.008055	267.3
0.063777	19.311	165.15	−0.006526	254.2
0.046139	14.027	164.79	−0.004844	242.7
0.032189	9.808	164.79	−0.003463	232.7

tions by the Debye-Hückel equation

$$^{\phi}Y = {}^{\phi}Y^{\circ} + A_Y\omega^{3/2}m^{1/2} + B_Y\omega m \qquad (14.2)$$

in which B_Y is an adjustable parameter and $\bar{Y}_2^{\circ}$ is the value of $^{\phi}Y$ at infinite dilution. The valence factor (ω) is related to molality (m), ionic charge (z_i), and molal ionic strength (I) by

$$I = 0.5\sum m_i z_i^2 = \omega m \qquad (14.3)$$

The values of the Debye-Hückel slopes (A_Y) were taken from a recent (ANANTHASWAMY and ATKINSON, 1984) extended version of the earlier calculations by BRADLEY and PITZER (1979): $A_V = 1.8743$ cm^{3}kg$^{1/2}$mol$^{-3/2}$ and $A_C = 32.783$ J K^{-1}kg$^{1/2}$mol$^{-3/2}$ at 25°C.

Equations of type 14.2 were fitted to the experimental results ($^{\phi}C_p$, $^{\phi}V$, and corresponding molalities, Table 14.1) to obtain the values $\bar{C}_{p,2}^{\circ}$, B_C, $\bar{V}_2^{\circ}$, and B_V that are listed in Table 14.2. To illustrate the accurate fits of equations of type (14.2), graphs of $^{\phi}Y$ - $A_Y\omega^{3/2}m^{1/2}$ against m are shown in Figure 14.1. Total (calorimetry, densimetry, chemicals, calculations) uncertainties in $\bar{C}_{p,2}^{\circ}$ and $\bar{V}_2^{\circ}$ values are approximately $\pm$ 6 J K^{-1}mol^{-1} and $\pm$ 0.5 cm^{3}mol^{-1}.

For thermodynamic calculations relevant to the infinite dilution reference state, $\bar{C}_{p,2}^{\circ}$ and $\bar{V}_2^{\circ}$ values are needed; these values are equal to the corresponding apparent and partial molar properties at infinite dilution (see eq. 14.4 below). But most equilibrium and enthalpy data that are presently available for aqueous EDTA systems were obtained from results of measurements at constant ionic strength, usually 0.1 molar. It is therefore appropriate to use the present results to calculate partial molar properties ($\bar{Y}_2$) at a corresponding ionic strength (0.033 molal Na_2MEDTA) by way of

$$\bar{Y} = {}^{\phi}Y + I\left(\frac{\partial {}^{\phi}Y}{\partial I}\right) \qquad (14.4)$$

Results of these calculations are given in Table 14.3.

For some thermodynamic calculations it is most convenient to work with conventional partial molar properties for individual ions, based on $\bar{Y}_2^{\circ}$ or $\bar{Y}_2^{\dagger}$ at I = 0.1 both equal to zero for H^+(aq). In Table 14.4 conventional properties for $SrEDTA^{2-}$(aq) and $BaEDTA^{2-}$(aq) as investigated here, and values for several other ions are listed.

Table 14.2: Standard state (infinite dilution) partial molar heat capacities, volumes, and $B_Y\omega$ parameters at 25.0°C.*

Solute	${}^{\phi}C_p^{\circ}$ (J $K^{-1}mol^{-1}$)	B_C (J kg $K^{-1}mol^{-2}$)	${}^{\phi}V^{\circ}$ (cm^3mol^{-1})	B_V ($cm^3kg\ mol^{-2}$)
$Na_2SrEDTA$	141.8 ± 0.8	247.0 ± 11	158.82 ± 0.05	10.51 ± 0.52
$Na_2BaEDTA$	192.1 ± 1.0	309.7 ± 13	162.54 ± 0.14	2.13 ± 2.6

* The $\pm$ values are the statistical uncertainties (standard deviations) associated with the fit of equations of type (14.2) to the experimental results. Total uncertainties are larger than these $\pm$ values, as discussed in the text.

Table 14.3: Partial molar properties at I = 0.10 (0.033 molal Na_2MEDTA) at 25.0°C.

Solute	$\bar{C}^{\dagger}_{p,2}$ (J $K^{-1}mol^{-1}$)	$\bar{V}^{\dagger}_{2}$ cm^3mol^{-1}
Na_2SrEDTA	204.9	162.19
Na_2BaEDTA	259.4	165.35

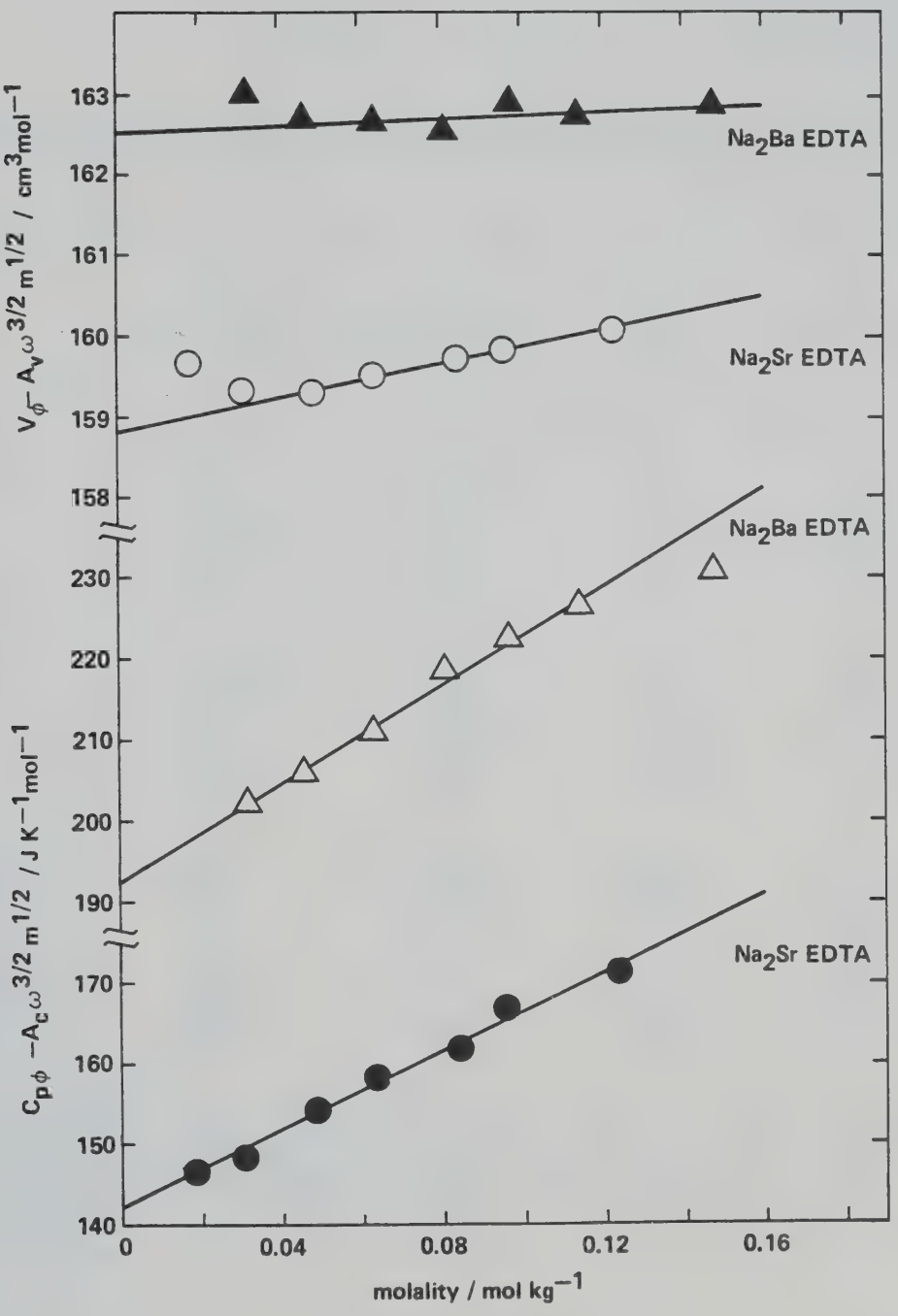

Figure 14.1: ${}^{\phi}V$ and ${}^{\phi}C_p$ minus the Debye-Hückel limiting terms for $BaEDTA^{2-}$(aq) and $SrEDTA^{2-}$(aq). Lines are least squares fits of eq. 14.2.

Table 14.4: Conventional partial molar properties for ions at I=0 (°) and I= 0.1 (†).*

Ion	$\bar{C}^{\circ}_{p,2}$ (J K^{-1}mol^{-1})	$\bar{C}^{\dagger}_{p,2}$ (J K^{-1}mol^{-1})	$\bar{V}^{\circ}_{2}$ (cm^{3}mol^{-1})	$\bar{V}^{\dagger}_{2}$ (cm^{3}mol^{-1})
H^+	0	0	0	0
Na^+	42.8	46.2	−1.21	−1.08
Cl^-	−127.2	−113.7	17.89	18.55
ClO_4^-	−27.1	−10.3	44.21	44.95
Mg^{2+}	−11.5	−8.5	−21.9	−25.0
Ca^{2+}	−22.6	−18.8	−17.6	−18.6
Sr^{2+}	−34.8	−24.6	−17.52	−16.78
Ba^{2+}	−45.6	−33.8	−12.80	−11.68
H_2EDTA^{2-}	83.2	129.4	156.73	159.11
$MgEDTA^{2-}$	111.3	156.8	162.93	165.40
$CaEDTA^{2-}$	95.4	143.2	158.51	161.08
$SrEDTA^{2-}$	56.2	112.5	161.24	164.35
$BaEDTA^{2-}$	106.5	167.0	164.96	167.51

* Values for $SrEDTA^{2-}$ and $BaEDTA^{2-}$ are from this work, while those for other ions are from HOVEY and TREMAINE (1985), DESNOYERS *et al.* (1976), PICKER *et al.* (1974), PERRON *et al.* (1974), TREMAINE *et al.* (1986), SINGH *et al.* (1977), ROUX *et al.* (1978).

14.4 Equilibrium calculations

As mentioned previously, equilibrium constants and enthalpies of various metal ion-EDTA complexation reactions are available for temperatures at or near 25°C. These quantities can be used in

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \tag{14.5}$$

for calculation of new values of the equilibrium constant over narrow ranges of temperature. A principal point of the present research was to obtain ΔC_p° values that can be used in eq. 14.5 and

$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_p = \Delta C_p^\circ \tag{14.6}$$

for similar calculations over much wider ranges of temperature. Because the equilibrium constants and enthalpies are based on a standard state having ionic strength equal to 0.1 rather than the usual infinite dilution state, the equations are written with superscript † instead of *o* as above.

Because there are no experimental data that describe the temperature dependence of $\Delta C_p^\dagger$ for the reactions under consideration here, eq. 14.6 was integrated taking $\Delta C_p^\dagger$ to be independent of temperature and then substituted into eq. 14.5, which was then integrated to yield

$$\begin{aligned} \ln K_T^\dagger \;=\; & \ln K_{298}^\dagger - \frac{\Delta H_{298}^\dagger}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right) + \\ & \frac{\Delta C_p^\dagger}{R}\left[\ln\left(\frac{T}{298.15}\right) + \frac{298.15}{T} - 1\right] - \frac{\Delta V^\dagger}{RT}(p-1) \end{aligned} \tag{14.7}$$

It is known that partial molar heat capacities of aqueous ions increase slowly with increasing temperature from below 25°C up to some higher temperature in the range from about 50 to 100°C, and then decrease with further increases in temperature. This decrease in $\bar{C}_{p,2}^\circ$ with rising temperature becomes increasingly steep at temperatures well above about 100°C. Because of the temperature dependence of the heat capacities of ions, eq. 14.7 is unlikely to be accurate for all ionic reactions at temperatures higher than about 100°C. However, it has been shown (LINDSAY, 1980; MURRAY and COBBLE, 1980; BARBERO *et al.*, 1982, 1983) that ΔC_p° and $\Delta C_p^\dagger$ are nearly independent of temperature over wide ranges of temperature for "isocoulombic" reactions (reactions that are symmetrical with respect to number

and charges of ions). Therefore, eq. 14.7 should be accurate for such reactions over a much wider range of temperature (up to about 200°C).

Complexation of metal ions with EDTA is most often done using the commercially available Na_2H_2EDTA, as represented by the following reaction equation

$$M^{2+}(aq) + H_2EDTA^{2-}(aq) = MEDTA^{2-}(aq) + 2H^+(aq) \qquad (14.8)$$

The thermodynamic properties for reactions of type 14.8 at T = 298.15 K and I = 0.1 for this reaction with M^{2+} = Sr^{2+}, Ba^{2+}, Ca^{2+}, and Mg^{2+} are listed in Table 14.5. $\Delta C_p^\dagger$ values can be used from the present work and earlier work (HOVEY and TREMAINE, 1985) in combination with already known thermodynamic properties listed in Table 14.5 to calculate equilibrium constants for reactions of type 14.8 at various temperatures. Reaction 14.8, however, is not isocoulombic, which means that calculations with equation 14.7 are unlikely to be reliable for temperatures far above about 100°C.

Equilibrium constants for reactions of type 14.8 provide information about the stabilities of $MEDTA^{2-}(aq)$ ions relative to $H_2EDTA^{2-}(aq)$, but it is generally more useful to have equilibrium constants that indicate relative stabilities of EDTA complexes of different metal ions. We therefore consider reactions of the type

$$M^{2+}(aq) + CaEDTA^{2-}(aq) = MEDTA^{2-}(aq) + Ca^{2+}(aq) \qquad (14.9)$$

as a way to make useful comparisons of the stabilities of $MEDTA^{2-}(aq)$ ions with stabilities of $CaEDTA^{2-}(aq)$ ions. It should also be noted that reactions represented by equation 14.9 are isocoulombic, which means that calculations with temperature independent $\Delta C_p^\dagger$ values can be expected to be usefully accurate over wide ranges of temperature as discussed previously. Results of these equilibrium calculations are summarized in Table 14.6.

14.5 Discussion

One of the purposes of the present work was to extend the data base for aqueous metal-ion EDTA complexes, with the further intention of developing improved correlation and prediction methods. The Born equation for the free energy change associated with hydration of an ion in a solvent assumed to be represented by a uniform

Table 14.5: Selected thermodynamic properties at I=0.1 for alkaline earth metal reaction with $H_2EDTA^{2-}(aq)$ as $M^{2+}(aq)$ + $H_2EDTA^{2-}(aq)$ = 2H+(aq) + $MEDTA^{2-}(aq)$.*

$M^{2+}(aq)$	$\log K^{\dagger}$	$\Delta H^{\dagger}$ (kJ mol^{-1})	$\Delta S^{\dagger}$ (J $K^{-1}mol^{-1}$)	$\Delta \bar{C}_p^{\dagger}$ (J $K^{-1}mol^{-1}$)	$\Delta \bar{V}_2^{\dagger}$ (cm^3mol^{-1})
Mg^{2+}	−7.56	56.5	44.7	35.9	31.3
Ca^{2+}	−5.78	15.3	−59.4	32.6	20.6
Sr^{2+}	−7.71	25.9	−60.7	7.7	20.1
Ba^{2+}	−8.59	21.5	−92.3	71.4	22.0

* All of the values listed above for Ca and Mg came from HOVEY and TREMAINE (1985). Values of $\log K^{\dagger}_{298}$ for Sr and Ba were taken directly from MARTELL and SMITH (1974). The listed $\Delta H^{\dagger}$ values for Sr and Ba have been obtained from appropriate combinations and averages of calorimetric results reported in VASIL'EV *et al.* (1976, 1978), ANDEREGG (1963), CHARLES (1954), CARE and STAVELEY (1956), and WRIGHT *et al.* (1965) and $\Delta S^{\dagger}$ values were obtained from $-RT \ln K^{\dagger}_{298}$ = $\Delta H^{\dagger} - T\Delta S^{\dagger}$. The $\Delta C_p^{\dagger}$ and $\Delta V^{\dagger}$ values for Sr and Ba are from this work.

Table 14.6: Calculated equilibrium constants for the reaction $M^{2+}(aq) + CaEDTA^{2-}(aq) = MEDTA^{2-}(aq) + Ca^{2+}(aq)$.

	$\log K^{\dagger}$		
t ($^{\circ}C$)	Mg^{2+}	Sr^{2+}	Ba^{2+}
0	−2.44	1.76	2.72
20	−1.90	1.90	2.79
25	−1.78	1.93	2.81
37	−1.50	2.00	2.85
50	−1.22	2.07	2.90
75	−0.74	2.18	2.99
100	−0.33	2.27	3.08
125	0.04	2.35	3.16
150	0.36	2.41	3.24
175	0.65	2.46	3.32
200	0.91	2.50	3.40

static dielectric constant can be used to estimate electrostatic contributions to the partial molar volumes and heat capacities investigated here. If the thermodynamic properties can be represented as the sum of electrostatic and non-electrostatic components after conversion of these properties to an absolute scale [where the properties of H^+(aq) are now not necessarily equal to zero], the non-electrostatic components can be calculated by using the Born equation and values for $\bar{Y}^{abs}(H^+)$. The absolute properties can be represented by

$$\bar{Y}^{abs} = \bar{Y}^{abs}_{elect} + \bar{Y}^{abs}_{non-elect} \tag{14.10}$$

Choosing absolute properties for H^+(aq) as chosen by HOVEY and TREMAINE (1985) leads to

$$\bar{V}^{abs}_{2,non-elect} = \bar{V}^{\circ}_2 - 5.5z + 1.03z^2 \tag{14.11}$$

$$\bar{C}^{abs}_{p,2,non-elect} = \bar{C}^{\circ}_{p,2} - 63z + 16.2z^2 \tag{14.12}$$

A graph of these non-electrostatic heat capacities against volumes is shown in Figure 14.2. The new results fall into the same overall grouping as those reported previously by HOVEY and TREMAINE (1985). The EDTA chelates whose geometries are not controlled by ligand field effects have slightly smaller volumes than those of divalent cobalt, nickel, copper, and zinc, which form octahedral complexes. Factors affecting the heat capacities and volumes of several EDTA-metal ions are discussed further in Chapter 17.

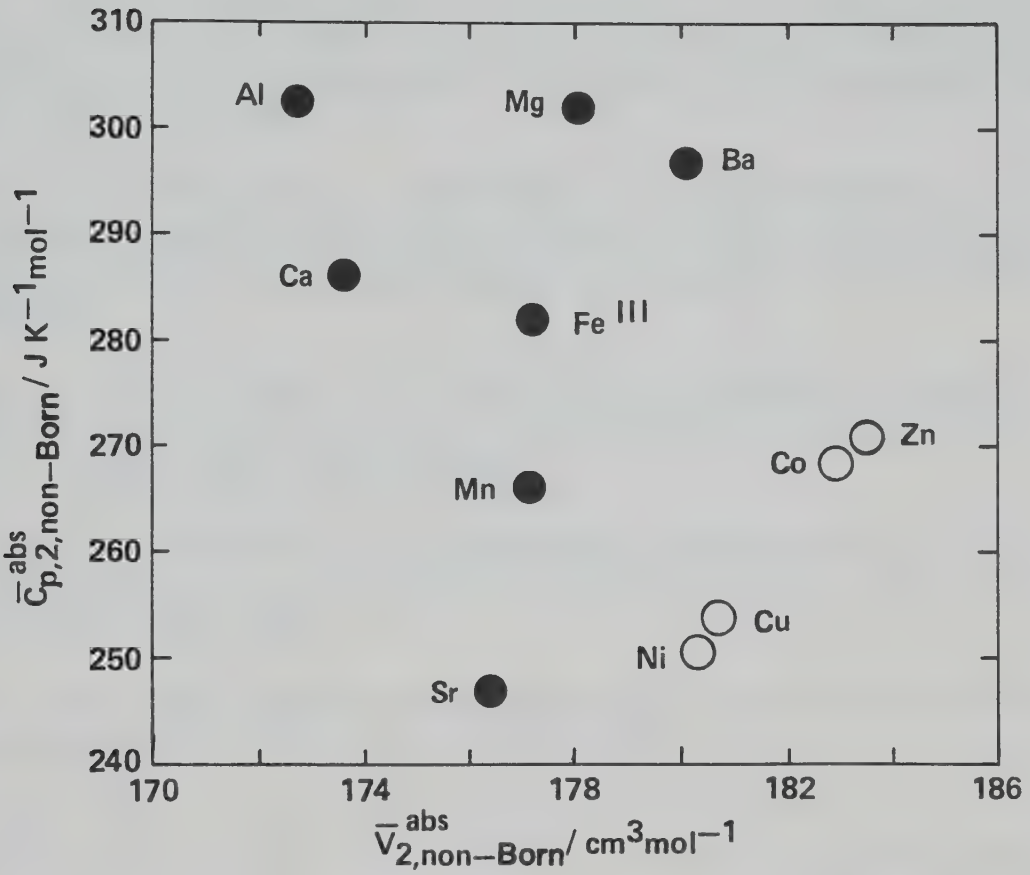

Figure 14.2: Partial molar heat capacities and volumes of EDTA complexes on the "absolute" ionic scale after subtraction of the Born contributions.

14.6 References

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Chapter 15

Thermodynamics of aqueous EDTA systems : Apparent and partial molar heat capacities and volumes of aqueous cadmium, mercury, and lead EDTA[1]

15.1 Introduction

As a further investigation of the thermodynamics of reactions involving aqueous complexes of EDTA (ethylenediaminetetraacetic acid), heat capacities and densities of aqueous solutions of $Na_2CdEDTA$, $Na_2HgEDTA$, and $Na_2PbEDTA$ have been measured at 25°C.

Aqueous solutions of EDTA are used as sequestering agents in industrial applications that include cleaning boilers, softening boiler and process water, treating oil wells to remove scales minerals, and decontaminating nuclear reactor systems. There are also medicinal uses of EDTA that include treating Alzheimer's disease by complexation of aluminum (YAEGER, 1983), treating ulcers (PUSCAS *et al.*, 1980), treating periarthritis and similar ailments (GUAZZOTTI, 1986), and as agents for increased contrast in NMR body imaging (RUNGE *et al.*, 1984). Specific to the salts studied in this paper is the use of EDTA to remove cadmium, mercury, and lead (BOSCOLO *et al.*, 1983) from the body. EDTA treatment of metal poisoning may introduce risks (WEDEEN *et al.*, 1983), but its wide versatility in the complexation of many heavy metal ions [including plutonium (CATSCH, 1968)] makes it a valuable chemical treatment (JONES and PRATT, 1976; COOPER, 1955).

As mentioned in Chapter 14 and by HOVEY and TREMAINE (1985), different investigators who have made measurements leading to equilibrium constants have

[1] A version of this Chapter has been accepted for publication. Hovey, J.K.; Hepler, L.G. *Inorganic Chemistry.*

generally obtained results in satisfactory agreement with each other. On the other hand, there is less good agreement between the results of different investigators who have reported enthalpies of complexation reactions, especially when enthalpies have been determined by way of equilibrium constants at several temperatures and the van't Hoff equation. Most of the uncertainties and possible errors in these ΔH values are due to the magnification of errors and uncertainties associated with differentiation $[(d \ln K/dT)_p]$ and to problems connected with the fact that EDTA forms weak complexes with most cations in supporting electrolytes (see Chapter 16). It therefore follows that ΔC_p° values obtained by double differentiation of $K = f(T)$ results or single differentiation of calorimetric $\Delta H^\circ = f(T)$ results will have large uncertainties. As previously recognized, the "best" ΔC_p° values are usually obtained by way of direct calorimetric measurements of heat capacities.

Although the complexation equilibria of Cd^{2+}, Hg^{2+}, and Pb^{2+} with EDTA have been investigated extensively near 25°C, there have been no investigations of these systems at the high temperatures that are important for several applications. One of the purposes of the present research has been to make calorimetric measurements of heat capacities of solutions that will lead to ΔC_p values for the various complexation equilibria, with these ΔC_p values to be used in calculating equilibrium constants and other thermodynamic properties that are applicable to solutions at high temperatures. Because of the way in which we have measured heat capacities, we have also obtained densities of solutions that have led to apparent and partial molar volumes and thence to values of ΔV for these same complexation equilibria and related thermodynamic properties. These ΔV values can be used in calculating the pressure dependence of complexation equilibria and related thermodynamic properties.

15.2 Experimental

Water used for all solutions was distilled, then passed through a Milli-Q reagent grade mixed bed ion exchange and activated carbon system, to yield water with a final resistance of 18 MΩ cm or greater. Standard solutions of NaCl were prepared by mass after drying the salt (Fisher certified, ACS) at 120°C for several hours.

$Na_2CdEDTA$ (ICN Pharmaceuticals) and $Na_2PbEDTA$ (Tokyo Kasei, certified

>99%) were recrystallized twice by a method identical to that described in Chapter 14. $Na_2HgEDTA$ was prepared by adding $Hg(NO_3)_2$ (Fisher, ACS) dissolved in dilute HNO_3(aq) to a solution of Na_2H_2EDTA (Fisher certified, ACS) until a slight excess of $Hg(NO_3)_2$ was present. Dilute NaOH was used to raise the pH of the solution slightly after each addition of $Hg(NO_3)_2$. Crystals were precipitated by dilution with ethanol and were then recrystallized twice as for the Cd and Pb EDTA complexes. All salts were dried at 60°C for three days. Stock solutions of the salts were prepared by mass from these dried (but still hydrated) salts. Total water contents of the dried $Na_2CdEDTA$ and $Na_2PbEDTA$ salts were obtained from mass loss on complete dehydration at 150°C under vacuum, with results that agreed with the amount calculated from elemental analyses of these salts. However, the $Na_2HgEDTA$ salt was found to decompose at 150°C, and the total water content for this salt was determined solely from the elemental analysis. The empirical formulas of these salts were found to be $Na_2CdEDTA \cdot 4.22\ H_2O$, $Na_2HgEDTA \cdot 2.68\ H_2O$, and $Na_2PbEDTA \cdot 1.09\ H_2O$.

Heat capacities of all solutions were measured at 25.00 ± 0.01°C with a Picker flow microcalorimeter (PICKER *et al.*, 1971). The specific heat capacity of water was taken from KELL (1972) and had the value 4.1793 J $K^{-1}g^{-1}$. Small corrections ($f = 1.006$) to the raw heat capacity data were made to allow for heat losses in the calorimeter, as described in Chapter 2 (DESNOYERS *et al.*, 1976). Densities of all solutions were measured relative to water at 25.00 ± 0.01°C with a Sodev 03D vibrating tube densimeter (PICKER *et al.*, 1974), which was calibrated with water and standard NaCl solutions. The density of water at 25°C was taken from KELL (1967) and had the value 0.997047 g cm^{-3}. The densities of the standard NaCl solutions were obtained from the results of PICKER *et al.* (1974). Temperature control for the densimeter and calorimeter was achieved with separate Sodev CT-L circulating baths (constant to ± 0.001°C). Temperatures of the baths were monitored with thermistors that had been calibrated against a Hewlett-Packard 2804A quartz thermometer.

15.3 Results

It is convenient to express results of the heat capacity and density measurements as apparent molar properties defined by

$$^{\phi}Y = \frac{Y_{sol} - n_1 Y_1^{\circ}}{n_2} \tag{15.1}$$

in which Y_{sol} is the extensive property (heat capacity or volume) of a specified quantity of solution, Y_1° is the property (heat capacity or volume) of one mole of water, and n_1 and n_2 are the amounts (moles) of water and of solute in the specified quantity of solution. This equation written specifically for the calculation of apparent molar volumes and heat capacities has the forms:

$$^{\phi}V = \frac{\frac{1+mM}{d} - \frac{1}{d_1^{\circ}}}{m} \tag{15.2}$$

$$^{\phi}C_p = \frac{c_p(1+mM) - c_{p,1}^{\circ}}{m} \tag{15.3}$$

Here m is the molality of the solution, M is the molar mass of the solute, d_1° and $c_{p,1}^{\circ}$ are the density and specific heat capacity of pure water, and d and c_p are the density and specific heat capacity of the solution. The $C_{p,\phi}$ and V_{ϕ} results are listed in Table 15.1 along with the direct experimental results for $d - d_1^{\circ}$ and $\left(\frac{c_p d}{c_{p,1}^{\circ} d_1^{\circ}} - 1\right)$.

The stability constants for the aqueous cadmium, mercury, and lead EDTA complexes are sufficiently large that these solutions can be regarded as 2:1 electrolytes of the type $2Na^+(aq) + MEDTA^{2-}(aq)$.

Apparent molar properties can be represented to moderate ionic strengths by the Debye-Hückel equation

$$^{\phi}Y = {}^{\phi}Y^{\circ} + A_Y \omega^{3/2} m^{1/2} + B_Y \omega m \tag{15.4}$$

in which B_Y is an adjustable parameter and $^{\phi}Y^{\circ}$ is the value of $^{\phi}Y$ at infinite dilution. The valence factor (ω) is related to the molality (m), charge (z_i), and molal ionic strength (I) by

$$I = \frac{1}{2}\sum m_i z_i^2 = \omega m \tag{15.5}$$

The values of the limiting law slopes (A_Y) (BRADLEY and PITZER, 1979) were taken from ANANTHASWAMY and ATKINSON (1984): $A_V = 1.8743$ cm^{3}kg$^{1/2}$mol$^{-3/2}$ and $A_C = 32.783$ J K^{-1}kg$^{1/2}$mol$^{-3/2}$ at 25°C.

Table 15.1: Results of calorimetric and densimetric measurements at 25.0°C.

m (mol kg^{-1})	$10^2(d - d_1^\circ)$ (g cm^{-3})	$^\phi V$ (cm^3 mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	$^\phi C_p$ (J K^{-1}mol^{-1})
		$Na_2CdEDTA$		
0.2014	5.3847	169.76	−2.090	256.4
0.1641	4.4311	168.74	−1.762	239.5
0.1321	3.6019	167.63	−1.454	225.8
0.1073	2.9464	166.88	−1.198	217.9
0.07021	1.9440	166.13	−0.811	201.4
0.04778	1.3351	164.64	−0.560	189.4
0.03001	0.8433	163.84	−0.359	177.9
		$Na_2HgEDTA$		
0.1881	6.6109	171.51	−1.617	341.9
0.1483	5.2590	170.71	−1.345	320.7
0.1257	4.4800	170.07	−1.176	307.0
0.09848	3.5328	169.49	−0.962	289.1
0.06820	2.4609	169.01	−0.697	269.7
0.03973	1.4452	168.05	−0.417	260.0
0.02778	1.0117	167.65	−0.294	251.7
		$Na_2PbEDTA$		
0.2552	8.7877	180.62	−2.920	259.8
0.2062	7.1733	180.14	−2.399	243.8
0.1703	5.9710	179.45	−2.032	230.9
0.1202	4.2602	178.88	−1.483	216.0
0.09009	3.2140	178.37	−1.131	207.2
0.06292	2.2611	177.45	−0.807	194.3
0.03440	1.2440	177.04	−0.451	183.9

Equation 15.4 was fitted to the experimental results (${}^{\phi}C_p$, ${}^{\phi}V$, and corresponding molalities in Table 15.1), leading to the values of ${}^{\phi}C_p^{\circ}$, B_C, ${}^{\phi}V^{\circ}$, and B_V that are listed in Table 15.2. Figures 15.1 and 15.2 show graphs of ${}^{\phi}Y$ - $A_Y\omega^{3/2}m^{1/2}$ against m as suggested by eq 15.4. Note that the values of the apparent molar properties at infinite dilution (${}^{\phi}C_p^{\circ}$, and ${}^{\phi}V^{\circ}$) are equal to the corresponding standard state partial molar quantities that are represented by $\bar{C}_{p,2}^{\circ}$ and $\bar{V}_2^{\circ}$. The values of $\bar{C}_{p,2}^{\circ}$ and $\bar{V}_2^{\circ}$ can be used to obtain values of ΔC_p° and ΔV° (conventional standard state based on properties of solutes at infinite dilution) for reactions involving the corresponding EDTA complexes.

Many previous investigations of EDTA complexes have been carried out with solutions maintained at constant ionic strength (often 0.1 molal or 0.1 molar) with an "inert" supporting electrolyte. To make the best use of the present results in combination with those from these earlier investigations, we have calculated partial molar properties at ionic strength 0.1 molal from our apparent molar properties and eq 15.4 by way of the equation

$$\bar{Y} = {}^{\phi}Y + I\left(\frac{\partial {}^{\phi}Y}{\partial I}\right) \tag{15.6}$$

Results of these calculations are given in Table 15.3.

Subsequent calculations in this chapter require partial molar properties for $Na_2CdEDTA$, $Na_2HgEDTA$, and $Na_2PbEDTA$ listed in Table 15.3 as well as values for several other species. It is convenient to do all of these calculations with conventional standard state properties for ions based on ${}^{\phi}Y^{\circ}(H^+, aq) \equiv 0$. Table 15.4 lists these conventional standard state partial molar volumes and heat capacities (I = 0 and I = 0.1 molal) for all of the ions of present interest. The thermodynamic quantities that pertain to an ionic strength of 0.1 molal (or molar) are denoted by a superscript †. Values for the volumes and heat capacities of $CdEDTA^{2-}$(aq), $HgEDTA^{2-}$(aq), and $PbEDTA^{2-}$(aq) were calculated from the results listed in Table 15.2 and values for Na^+(aq) listed in Table 15.4. Values for the cationic species in Table 15.4 were derived from perchlorate results when possible (SPITZER *et al.*, 1978; Chapter 3), and also from other salts (HOVEY and TREMAINE, 1985; PICKER *et al.*, 1971; DESNOYERS *et al.*, 1976; PICKER *et al.*, 1974; Chapter 2; TREMAINE *et al.*, 1986; SINGH *et al.*, 1977; ROUX *et al.*, 1978).

Table 15.2: Standard state (infinite dilution) partial molar heat capacities, volumes, and $B_Y\omega$ parameters at 25.0°C.*

Solute	${}^{\phi}C_p^{\circ}$ (J $K^{-1}mol^{-1}$)	B_C (J kg $K^{-1}mol^{-2}$)	${}^{\phi}V^{\circ}$ (cm^3mol^{-1})	B_V ($cm^3kg\ mol^{-2}$)
$Na_2CdEDTA$	143.3 ± 1.2	172.7 ± 9.7	161.60 ± 0.04	19.06 ± 0.34
$Na_2HgEDTA$	200.7 ± 1.1	361.3 ± 8.4	165.82 ± 0.12	7.423 ± 0.99
$Na_2PbEDTA$	148.0 ± 1.4	82.35 ± 11	175.08 ± 0.12	2.654 ± 0.76

* The $\pm$ values are the standard deviations associated with the fit of eq 15.4 to the experimental results. Total uncertainties (calorimetric, densimetric, chemicals, and extrapolations) are about $\pm$ 6 J $K^{-1}mol^{-1}$ and $\pm$ 0.6 cm^3mol^{-1}.

Table 15.3: Partial molar properties at $I = 0.10$ (0.033 molal Na_2MEDTA) at 25.0°C.

Solute	$\bar{C}^{\dagger}_{p,2}$ (J $K^{-1}mol^{-1}$)	$\bar{V}^{\dagger}_{2}$ cm^3mol^{-1}
$Na_2CdEDTA$	201.46	165.54
$Na_2HgEDTA$	271.42	168.98
$Na_2PbEDTA$	200.09	177.92

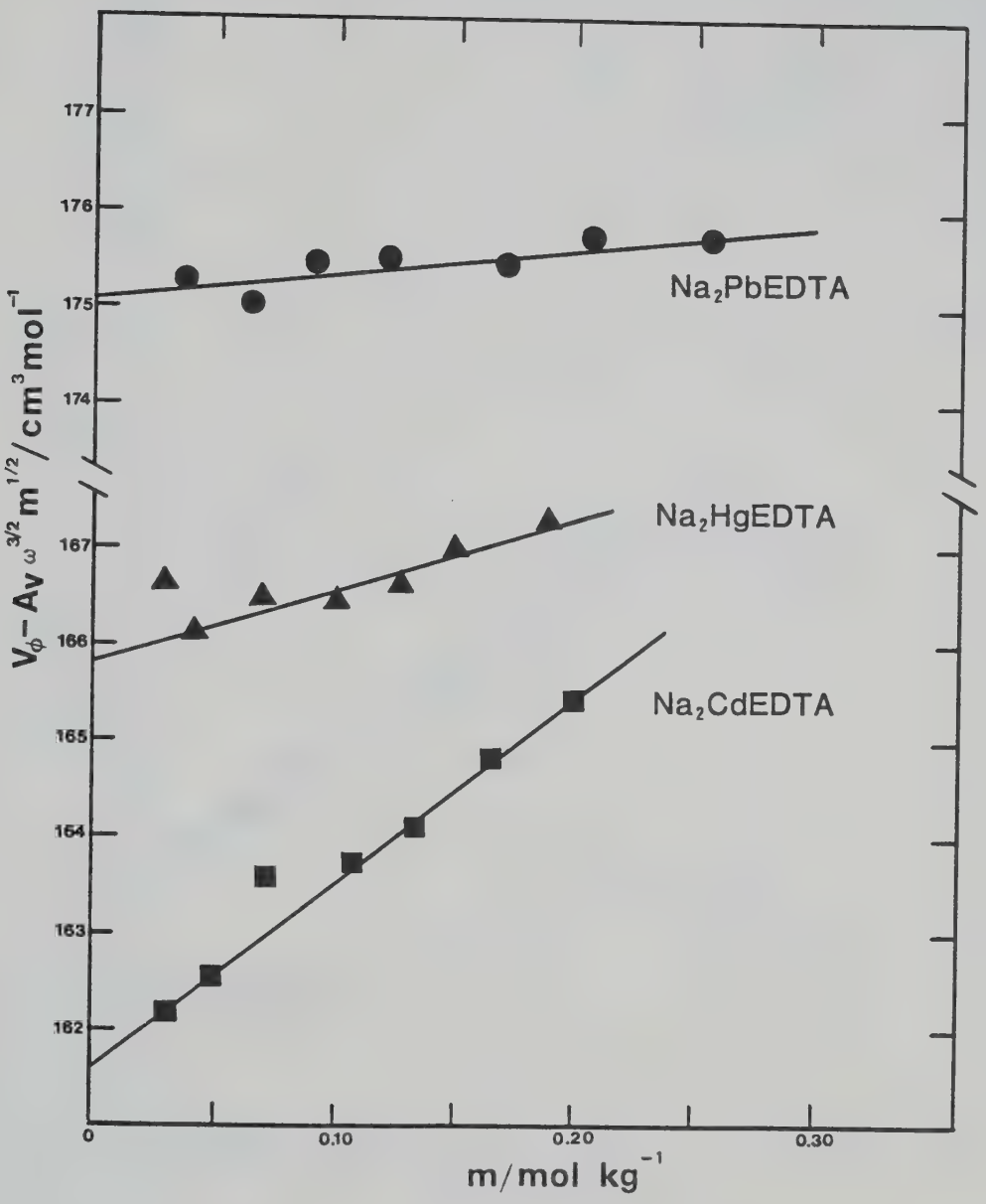

Figure 15.1: Apparent molar volumes minus the Debye-Hückel limiting law ($A_V \omega^{3/2} m^{1/2}$) for $Na_2CdEDTA(aq)$, $Na_2HgEDTA(aq)$ and $Na_2PbEDTA(aq)$. Lines are least squares fits of eq 15.4.

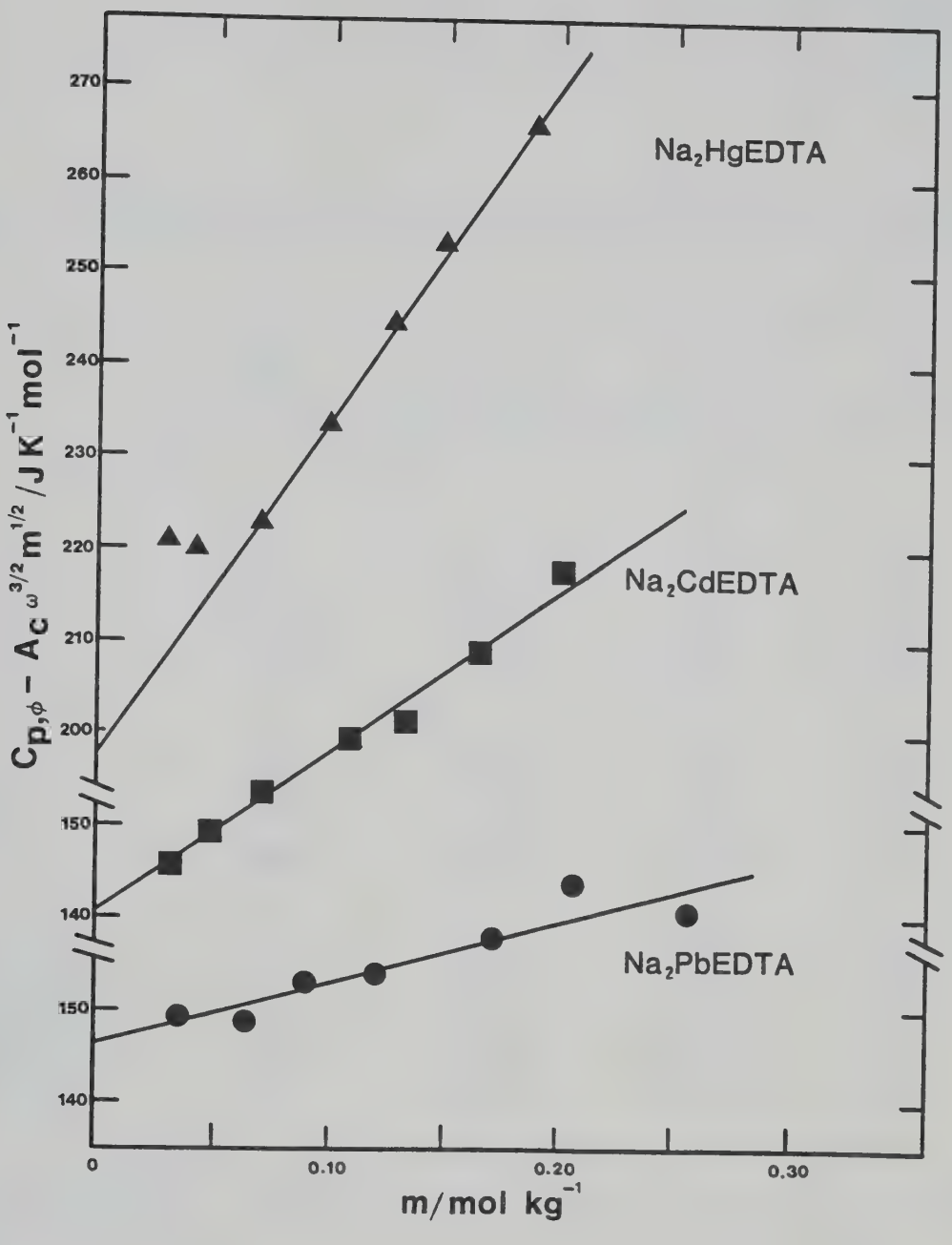

Figure 15.2: Apparent molar heat capacities minus the Debye-Hückel limiting law ($A_C\omega^{3/2}m^{1/2}$) for $Na_2CdEDTA(aq)$, $Na_2HgEDTA(aq)$ and $Na_2PbEDTA(aq)$. Lines are least squares fits of eq 15.4.

Table 15.4: Conventional partial molar properties for ions at I=0 (°) and I= 0.1 (†).*

Ion	$\bar{C}^{\circ}_{p,2}$ (J $K^{-1}mol^{-1}$)	$\bar{C}^{\dagger}_{p,2}$ (J $K^{-1}mol^{-1}$)	$\bar{V}^{\circ}_{2}$ (cm^3mol^{-1})	$\bar{V}^{\dagger}_{2}$ (cm^3mol^{-1})
H^+	0	0	0	0
Na^+	42.8	46.2	−1.21	−1.08
Cl^-	−127.2	−113.7	17.89	18.55
ClO_4^-	−25.5	−9.9	43.99	44.64
Ca^{2+}	−25.8	−19.5	−17.2	−16.0
Cd^{2+}	−6.4	−4.1	−14.2	−13.6
Hg^{2+}	−16.3	−3.4	−14.1	−13.2
Pb^{2+}	−56.0	−46.6	−17.7	−16.9
H_2EDTA^{2-}	83.2	129.4	156.73	159.11
$CaEDTA^{2-}$	95.4	143.2	158.51	161.08
$CdEDTA^{2-}$	57.7	109.1	164.02	167.70
$HgEDTA^{2-}$	115.1	179.0	168.24	171.14
$PbEDTA^{2-}$	62.4	107.7	177.50	180.08

* Values for $CdEDTA^{2-}$, $HgEDTA^{2-}$ and $PbEDTA^{2-}$ are derived from results in this chapter, while sources for the other ions are discussed in the text.

Equilibrium constants for the complexation reactions of $H_2EDTA^{2-}(aq)$ with $Cd^{2+}(aq)$, $Hg^{2+}(aq)$, and $Pb^{2+}(aq)$ as well as the corresponding enthalpy and entropy changes for these reactions are required in calculations that follow. Equilibrium constants have been selected from MARTELL and SMITH (1974) at 0.1 molar for the complexation reactions of $Cd^{2+}(aq)$, $Hg^{2+}(aq)$, and $Pb^{2+}(aq)$ with $EDTA^{4-}(aq)$, as represented by:

$$M^{2+}(aq) + EDTA^{4-}(aq) = MEDTA^{2-}(aq) \qquad (15.7)$$

Equilibrium constants associated with the complexation reactions of $H_2EDTA^{2-}(aq)$ with $Cd^{2+}(aq)$, $Hg^{2+}(aq)$, and $Pb^{2+}(aq)$ have been calculated from the data listed by ANDEREGG (1977) for the ionization of $H_2EDTA^{2-}(aq)$, and values from MARTELL and SMITH (1974) cited earlier. Reactions of this type are represented by

$$M^{2+}(aq) + H_2EDTA^{2-}(aq) = MEDTA^{2-}(aq) + 2H^{+}(aq) \qquad (15.8)$$

The $\Delta H^{\dagger}$ values associated with reaction 15.8 have been calculated for $M^{2+}(aq) = Cd^{2+}(aq)$, $Hg^{2+}(aq)$, and $Pb^{2+}(aq)$ from combinations and averages of the available calorimetric data for reactions represented by eq 15.7 and the enthalpies of ionization of $H_2EDTA^{2-}(aq)$ from VASIL'EV *et al.* (1978).

Enthalpies for reactions of type 15.7 were selected from CHRISTENSEN *et al.* (1975). Calculations involving $Cd^{2+}(aq)$ complexation have lead to $\Delta H^{\dagger} = -39.3 \pm 2$ kJ mol^{-1} as an average of results at 25°C (JORDAN and ALLEMAN, 1957; ANDEREGG, 1964; CHARLES, 1954; WRIGHT *et al.*, 1965) and 20°C (ANDEREGG, 1963; CARE and STAVELEY, 1956) after correction of the 20°C values to 25°C with the present heat capacity values, and the estimated heat capacity change for the ionization of $H_2EDTA^{2-}(aq)$ from VASIL'EV *et al.* (1978). Similar calculations involving $Hg^{2+}(aq)$ (ANDEREGG, 1964; WRIGHT *et al.*, 1965; ANDEREGG, 1963; MOELLER and CHU, 1966) and $Pb^{2+}(aq)$ (JORDAN and ALLEMAN, 1957; CHARLES, 1954; WRIGHT *et al.*, 1965; ANDEREGG, 1963; CARE and STAVELEY, 1956) have led to the values $\Delta H^{\dagger}$ = -77.6 ± 2 kJ mol^{-1} for Hg^{2+} and -57.6 ± 1 kJ mol^{-1} for Pb^{2+}. These values have been combined with enthalpies of ionization for $H_2EDTA^{2-}(aq)$ from VASIL'EV *et al.* (1978) to obtain the values listed in Table 15.5. Entropy changes associated with reactions represented by eq 15.8 have been calculated using the relationship $-RT \ln K^{\dagger} = \Delta H^{\dagger} - T\Delta S^{\dagger}$ and are listed in Table 15.5. The $\Delta C_p^{\dagger}$

and $\Delta V^\dagger$ values listed in Table 15.5 were calculated from the results given in Table 15.4. A critical evaluation of all of these thermodynamic data for the reactions discussed above is presented in Chapter 17 along with data for other EDTA systems.

15.4 Equilibrium calculations

As discussed previously, there are data available for the equilibrium constants and enthalpies associated with complexation of $Cd^{2+}(aq)$, $Hg^{2+}(aq)$, and $Pb^{2+}(aq)$ with $EDTA^{4-}(aq)$ at or near 25°C. These data can be used to calculate equilibrium constants over ranges of temperature using the van't Hoff equation and the Kirchoff equation:

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \tag{15.9}$$

$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_p = \Delta C_p^\circ \tag{15.10}$$

Partial molar volumes can be used to calculate equilibrium constants at elevated pressures by way of the equation

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta V^\circ}{RT} \tag{15.11}$$

Combination and integration of eqs 15.9-15.11, taking ΔC_p and ΔV to be independent of temperature and pressure, leads to

$$\begin{aligned} \ln K_T^\dagger \;=\; & \ln K_{298}^\dagger - \frac{\Delta H_{298}^\dagger}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right) + \\ & \frac{\Delta C_p^\dagger}{R}\left[\ln\left(\frac{T}{298.15}\right) + \frac{298.15}{T} - 1\right] - \frac{\Delta V^\dagger}{RT}(p-1) \end{aligned} \tag{15.12}$$

Eq. 15.12 is expected (LINDSAY, 1980; MURRAY and COBBLE, 1980) to be accurate over wide ranges of temperature and pressure for isocoulombic (same number and charge types of ions on both sides of reaction equation) reactions.

Most applications of EDTA involve the use of Na_2H_2EDTA adjusted to a pH value specific to each application. It is appropriate then to write the equations for reactions of various metal ions with $H_2EDTA^{2-}(aq)$ as in eq 15.8. Previous measurements of the heat capacity and volume for $H_2EDTA^{2-}(aq)$ (HOVEY and TREMAINE, 1985; Chapter 16) facilitate such calculations.

Table 15.5: Selected thermodynamic properties at $I = 0.1$ for heavy metal ion reactions with $H_2EDTA^{2-}(aq)$ as $M^{2+}(aq) + H_2EDTA^{2-}(aq) = 2H^+(aq) + MEDTA^{2-}(aq)$.*

$M^{2+}(aq)$	$\log K^\dagger$	$\Delta H^\dagger$ (kJ mol^{-1})	$\Delta S^\dagger$ (JK^{-1}mol^{-1})	$\Delta \bar{C}_p^\dagger$ (JK^{-1}mol^{-1})	$\Delta \bar{V}_2^\dagger$ (cm^{3}mol^{-1})
Ca^{2+}	−5.78	15.3	−59.4	33.3	18.0
Cd^{2+}	−0.03	3.0	9.5	−16.2	22.2
Hg^{2+}	5.11	−36.6	−24.9	53.0	25.2
Pb^{2+}	1.49	−11.8	−11.1	24.9	37.9

* The values listed above for Ca^{2+} came from Table 15.4. Other values are discussed in the text.

Medicinal and many other uses of EDTA that require limitation of the harsh sequestering ability of the uncomplexed salt use the calcium or zinc complex. It is also appropriate then to write equations for the exchange reactions with $CaEDTA^{2-}(aq)$:

$$M^{2+}(aq) + CaEDTA^{2-}(aq) = MEDTA^{2-}(aq) + Ca^{2+}(aq) \qquad (15.13)$$

Because the reactions represented by eq 15.13 are isocoulombic, this represents a favorable case for extrapolation to high temperatures and/or pressures. Equilibrium data for these exchange reactions permit useful comparisons of the stabilities of the $MEDTA^{2-}(aq)$ ions relative to $CaEDTA^{2-}(aq)$. Equilibrium constants have been calculated from the data listed in Table 15.5, using eq 15.12. Water saturation pressures above 100°C were used and were taken from HAAR *et al.* (1984). The results of these calculations are given in Table 15.6.

15.5 Discussion

In Chapter 14, the residual heat capacity against residual volume after subtraction of the Born (electrostriction) terms were plotted. It was found that all of the metal ion-EDTA complexes were packed into small groupings consistent with their coordination numbers and the effects of ligand field stabilization. The residual or non-electrostriction component is a large factor in determining the thermodynamic properties of such ions.

Spectroscopic studies (MCCONNELL *et al.*, 1978) have shown that the structures of many aqueous EDTA complexes are similar to those in the solid state. EDTA complexes of many cations do not have the most common six-coordinate geometry of EDTA complexes. Instead, one carboxylate of an EDTA molecule is detached from the metal ion, which usually results in coordination by a molecule of water. The resulting "quinquedentate" structure is common among many EDTA complexes. Many of the differences in the thermodynamic properties of EDTA complex ions are attributed to the relative distribution of quinquedentate and hexadentate structures (Chapter 14; HOVEY and TREMAINE, 1985; NUTTAL and STALKER, 1977). The standard state volumes (present work; Chapter 14; HOVEY and TREMAINE, 1985) for the complexes of EDTA with divalent Cd, Hg, Mn, Co, Ni, Cu, Zn, and Sr are all

Table 15.6: Calculated equilibrium constants for the reaction $M^{2+}(aq) + CaEDTA^{2-}(aq) = MEDTA^{2-}(aq) + Ca^{2+}(aq)$.

	$\log K^{\dagger}$		
t ($^{\circ}C$)	Cd^{2+}	Hg^{2+}	Pb^{2+}
0	5.94	11.73	7.70
20	5.79	11.05	7.35
25	5.75	10.89	7.27
37	5.66	10.54	7.09
50	5.58	10.19	6.90
75	5.41	9.60	6.58
100	5.26	9.09	6.31
125	5.11	8.65	6.06
150	4.97	8.26	5.84
175	4.84	7.92	5.65
200	4.71	7.62	5.47
250	4.48	7.11	5.03

consistent with the suggestion that these complexes are mixtures of quinquedentate and hexadentate structures. This suggestion is supported by spectra for several of these complexes in solution (McConnell and Nuttal, 1977).

The fact that the measured volume of the lead EDTA complex is significantly larger than those for the above mentioned ions is not simply due to the "large" size of Pb^{2+} since the radius of this ion is about 0.1 Å less than the radius of Ba^{2+} (and the volume of the complex ion is about 13 cm^3mol^{-1} larger. It has been suggested (McConnell *et al.*, 1978) that the non-bonding s-electrons of Pb^{2+} may influence the stereochemistry of this ion in solution. The observed eight-coordinate structure in the solid state (Harrison and Steel, 1982) is attributed to the formation of dimeric lead-EDTA units in which the the seventh coordination site involves a water molecule, and the eighth involves a neighbouring EDTA molecule. This result along with our present results suggests that the lead ion associated with EDTA prefers a large coordination number involving EDTA and two water molecules, which leads to a substantially larger total partial molar volume than for other complexes, including those known to form 7-coordinate structures (Nuttal and Stalker, 1977).

The standard state heat capacities are all influenced by the same factors as the standard state volumes, with additional contributions from relaxation effects due to the change in the distribution of structures with changes in temperature, as discussed by Ots (1973). It is evident that the standard state volumes and heat capacities are not sensitive to direct size-charge effects of the metal cation but rather to induced structural and coordinational changes of the EDTA molecule.

15.6 References

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Chapter 16

Thermodynamics of aqueous EDTA systems: Apparent and partial molar heat capacities and volumes of aqueous $EDTA^{4-}$, $HEDTA^{3-}$, H_2EDTA^{2-}, $NaEDTA^{3-}$, and $KEDTA^{3-}$ at 25°C. Relaxation effects in mixed aqueous electrolyte solutions and calculations of temperature dependent equilibrium constants[1]

16.1 Introduction

Aqueous solutions of EDTA (ethylenediaminetetraacetic acid) and its salts have found use in many applications, as discussed in Chapters 14 and 15. From the investigations described in Chapters 14 and 15, and the results of HOVEY and TREMAINE (1985), there is now a reasonably complete thermodynamic data base for aqueous complexes of EDTA with several cations. On the other hand, potentially valuable thermodynamic data for complexes of EDTA with some other important cations and for the acid dissociation species $HEDTA^{3-}(aq)$, and $EDTA^{4-}(aq)$ are lacking. The importance of the acid dissociation species of EDTA can be seen in Figure 16.1, where the speciation of EDTA solutions at 25°C as a function of pH at 0.1 molar ionic strength is illustrated (DANIELE *et al.*, 1985).

Thermodynamic measurements carried out with constant ionic strength media of alkali metal salts are complicated by the formation of alkali metal ion - EDTA complexes (MARTELL and SMITH, 1974; ANDEREGG, 1977). Similarly, investigations with the highly alkaline solutions that are required to obtain most of the EDTA as

[1] A version of this chapter has been published in a special issue of the *Canadian Journal of Chemistry* honouring the late Professor James A. Morrison: Hovey, J.K.; Hepler, L.G.; Tremaine, P.R. *Canadian Journal of Chemistry* **66**, 881- 896.

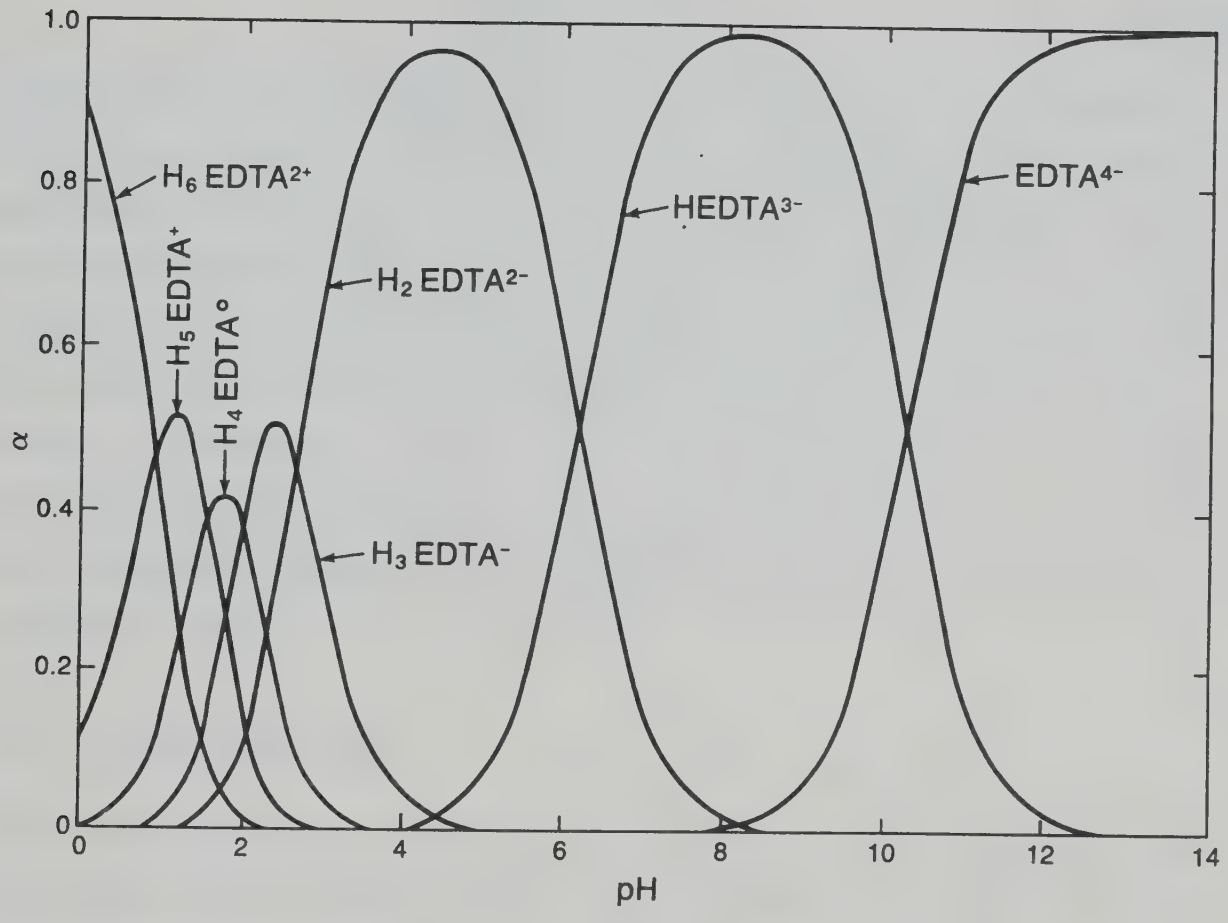

Figure 16.1: Speciation of aqueous EDTA at 25°C and I = 0.10 molar (DANIELE *et al.*, 1985).

the $HEDTA^{3-}$(aq) and $EDTA^{4-}$(aq) anions are also complicated by the formation of EDTA complexes with the cations that inevitably accompany hydroxide ions.

Several investigations of equilibrium constants and enthalpies of reaction involving solutions of EDTA have been carried out over a limited temperature range near 25°C, thereby permitting calculations of ΔC_p° values by way of

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \tag{16.1}$$

and

$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_p = \Delta C_p^\circ \tag{16.2}$$

Accurate values of ΔC_p° would allow both ΔH° and $\ln K$ to be extrapolated to temperatures beyond the range of the original measurements. Unfortunately, the magnification of errors and uncertainties associated with differentiation, and also the complications mentioned above, cause many ΔC_p° values from eq. 16.2 to have very large uncertainties. Calorimetric measurements of heat capacities have therefore been carried out as described in this Chapter. Densities have also been measured, leading to new apparent and partial molar volumes. Analysis of the resultant experimental data to obtain the desired standard state partial molar properties of specified ions is complicated because all of the solutions investigated have contained at least one cationic species and two anionic species.

16.2 Experimental

Water to be used for all experiments was filtered through activated charcoal and then passed through a Milli-RO4/Milli-Q reagent grade mixed bed ion exchange and activated carbon system to yield water with resistivity greater than 18 MΩ cm.

Solutions of NaCl (Fisher certified, ACS) were prepared by mass after drying the salt at 110°C for several hours. Crystalline H_4EDTA (Fisher certified, ACS) was dried at 140°C for several hours to yield material that has been described (SKOOG and WEST, 1976) as a primary standard. Aqueous solutions of NaOH (50%) and KOH (1 molar) were obtained from Fisher (certified, ACS). Aqueous solutions of $(CH_3)_4NOH$ (25%) were obtained from both Fisher (certified) and Alfa (certified purity 99.9999%). The solution from Alfa was used without further purification, but

the sample from Fisher was purified by passing it through an anion exchange column with resin in the hydroxide form to remove chloride and other anionic impurities. All hydroxide solutions were standardized by titration against potassium hydrogen phthalate. A solution of Na_2H_2EDTA was prepared by dissolving the salt (Fisher cerified, ACS) in pure water and then standardized by titration against standard solutions of zinc chloride (SKOOG and WEST, 1976). A solution of $[(CH_3)_4N][HEDTA]$ was prepared by adding a weighed amount of $(CH_3)_4NOH$ (Alfa) solution to a weighed amount of H_4EDTA, followed by adjustment to pH = 8.30 with a very dilute solution of $(CH_3)_4NOH$. Further solutions were prepared by dilution of this solution with very dilute $(CH_3)_4NOH$. Stock solutions of known stoichiometric compositions of $[(CH_3)_4N]_4EDTA + (CH_3)_4NOH$ (Alfa and Fisher), $Na_4EDTA + NaOH$, and $K_4EDTA + KOH$ were prepared by adding weighed amounts of standardized hydroxide solutions to weighed amounts of dried H_4EDTA. Further solutions were prepared by dilution with standardized hydroxide solutions. All of these alkaline solutions were prepared under nitrogen and then stored in nitrogen filled dessicators containing silica gel and ascarite pellets to minimize carbonate contamination.

Densities were measured relative to water at 25.00 ± 0.01°C with a Sodev 03D vibrating tube densimeter (PICKER *et al.*, 1974), which was calibrated with pure water and a standard solution of NaCl. Heat capacities were measured relative to water with a Sodev CP-C Picker flow microcalorimeter (PICKER *et al.*, 1974). Temperatures were controlled (constant to ± 0.001 °C) with a Sodev CT-L circulating bath and monitored with calibrated thermistors. The density and specific heat capacity of water at 25°C were taken from KELL (1967, 1972) and had the values 0.997047 g cm^{-3} and 4.1793 J $K^{-1}g^{-1}$, respectively. Daily evaluation of the calorimetric heat loss correction factor (DESNOYERS *et al.*, 1976; Chapter 2) by way of measurements on standard solutions of NaCl led to $f = 1.006 \pm 0.002$.

16.3 Results and calculations

16.3.1 $[(CH_3)_4]_4NEDTA$

The Picker vibrating tube densimeter and calorimeter measure $\left(\frac{c_p d}{c^\circ_{p,1} d^\circ_1} - 1\right)$ and $(d - d^\circ_1)$, in which c_p and $c^\circ_{p,1}$ are the specific heats of solution and of pure water, and d and

d_1° are the densities of solution and of pure water, respectively. It is most useful to express the experimental results for mixed electrolyte solutions of $[(CH_3)_4N]_4EDTA$ + $(CH_3)_4NOH$ as "experimental" apparent molar properties (${}^\phi V_\Sigma^{exp}$, ${}^\phi C_{p,\Sigma}^{exp}$) that are defined by

$$ {}^\phi Y_\Sigma^{exp} = \frac{Y_{sol} - n_1 Y_1^\circ}{n_2 + n_3} \tag{16.3} $$

Here, Y_{sol} is the extensive property (volume or heat capacity) of a specified quantity of solution, Y_1° is the property (volume or heat capacity) of one mole of pure solvent (water), and n_1, n_2, and n_3 are the amounts (moles) of water and of solutes 2 (M_4EDTA) and 3 (MOH) in the specified quantity of solution. For solutions containing molalities of solutes represented by m_2 and m_3, the equations that define ${}^\phi V_\Sigma^{exp}$ and ${}^\phi C_{p,\Sigma}^{exp}$ are given by

$$ {}^\phi V_\Sigma^{exp} = \frac{\frac{1 + m_2 M_2 + m_3 M_3}{d_{sol}} - \frac{1}{d_1^\circ}}{m_2 + m_3} \tag{16.4} $$

$$ {}^\phi C_{p,\Sigma}^{exp} = \frac{c_p(1 + m_2 M_2 + m_3 M_3) - c_{p,1}^\circ}{m_2 + m_3} \tag{16.5} $$

where M_2 and M_3 are the molar masses of the solutes. These experimental results are listed by Table 16.1.

At high pH values nearly all of the dissolved EDTA is in the $EDTA^{4-}(aq)$ form, as shown by Figure 16.1. There is evidence (DANIELE *et al.*, 1985), however, that $EDTA^{4-}(aq)$ at high concentrations of $(CH_3)_4NOH$ (> 0.1 molal) forms complexes or ion pairs (small stability constant) with $(CH_3)_4N^+(aq)$. Calculations of the speciation of the present solutions, with the assumption that the rather uncertain equilibrium constant is exactly correct, have shown that the amount of complex present is so small as to have negligible effect upon the results obtained by extrapolation to infinite dilution. Consequently, only the simpler calculations based on neglect of ion pair or complex formation of $(CH_3)_4N^+(aq)$ with $EDTA^{4-}(aq)$ are described here.

Because the high pH solutions in which most of the dissolved EDTA is in the form of $EDTA^{4-}(aq)$ contain two anionic species [the $EDTA^{4-}(aq)$ of present interest and also $OH^-(aq)$], it is necessary to make use of some model for the excess thermodynamic properties of mixed electrolyte solutions to permit extraction of the desired properties of $EDTA^{4-}(aq)$ from the experimental quantities defined by eq.

Table 16.1: Compositions of solutions and results of calorimetric and densimetric measurements.*

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^3(d - d_1^\circ)$ (g cm^{-3})	$^\phi V^{exp}$ (cm^3 mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	$^\phi C_p^{exp}$ ‡ (J K^{-1}mol^{-1})
		$[(CH_3)_4N]_4EDTA + (CH_3)_4NOH$ (Fisher)			
0.1132	0.00170	9.672	489.78	−3.207	803.7
0.09151	0.02149	8.059	417.26	−2.752	668.0
0.06943	0.04161	6.276	341.99	−2.275	536.3
0.04734	0.06174	4.501	263.60	−1.800	391.7
0.02509	0.08200	2.729	181.29	−1.243	257.2
0.01413	0.09199	1.838	139.68	−0.989	183.7
0.1166	0.08247	10.288	326.11	−3.733	518.3
0.1277	0.1715	11.587	260.78	−4.479	407.5
0.04269	0.1289	4.461	187.62	−2.008	273.1
0.04042	0.4014	5.670	123.10	−3.417	169.7
		$[(CH_3)_4N]_4EDTA + (CH_3)_4NOH$ (Alfa)			
0.1086	0.1126	9.564	288.24	−3.626	467.7
0.09517	0.1133	8.522	274.02	−3.279	442.4
0.08173	0.1139	7.437	258.11	−2.936	412.3
0.06871	0.1145	6.406	240.40	−2.607	376.9
0.06223	0.1148	5.858	230.82	−2.434	359.8
0.05146	0.1153	4.979	213.09	−2.153	325.5
0.04180	0.1158	4.185	195.23	−1.888	293.9
0.02934	0.1164	3.149	168.84	−1.544	246.7
0.02174	0.1167	2.498	150.65	−1.330	215.3
0.01195	0.1172	1.682	123.91	−1.043	171.1
		$Na_3[NaEDTA] + NaOH$			
0.2057	0.1609	51.485	85.84	−1.651	162.3
0.1744	0.1566	44.824	80.04	−1.485	139.8
0.1552	0.1539	40.720	75.77	−1.380	123.5
0.1321	0.1507	35.740	69.89	−1.240	103.2

Table 16.1: (continued)

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^3(d - d_1^\circ)$ (g cm^{-3})	$^\phi V^{exp}$ (cm^3 mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	$^\phi C_p^{exp}$ ‡ (J K^{-1}mol^{-1})
0.1168	0.1486	32.385	65.43	−1.141	88.7
0.09857	0.1461	28.360	59.28	−1.016	69.8
0.07562	0.1429	23.266	49.91	−0.852	42.3
0.05594	0.1402	18.812	40.18	−0.695	17.1
0.03969	0.1380	15.101	30.38	−0.556	−5.82
0.02053	0.1353	10.695	15.86	−0.392	−39.9
		K_3[KEDTA] + KOH			
0.2049	0.1763	58.085	106.23	−3.530	37.0
0.1456	0.1669	44.071	91.88	−2.748	2.03
0.1237	0.1635	38.767	85.02	−2.447	−13.2
0.08943	0.1580	30.346	71.55	−1.939	−37.5
0.05980	0.1533	22.835	56.54	−1.485	−61.2
0.03655	0.1497	16.894	40.80	−1.109	−82.7
0.01932	0.1469	12.381	26.31	−0.822	−99.4
0.1740	0.2763	56.943	75.34	−3.355	−9.87
0.1641	0.3423	56.207	67.12	−3.328	−5.96
0.01746	0.2302	15.936	18.71	−1.034	−98.3
0.01577	0.3046	19.132	15.09	−1.220	−98.0
		$[(CH_3)_4N]_3$[HEDTA]			
0.2194		17.944	423.29	−5.045	705.3
0.1710		14.248	423.32	−4.050	694.2
0.1299		10.999	423.31	−3.126	694.0
0.1299		11.017	423.17		
0.1078		9.233	423.12	−2.633	687.4
0.08617		7.447	423.08	−2.130	683.2
0.06433		5.632	422.72	−1.608	679.4
0.03648		3.237	422.56	−0.927	673.1
0.01649		1.481	422.22	−0.425	665.5

Table 16.1: (continued)

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	$10^3(d - d_1^\circ)$ (g cm^{-3})	${}^\phi V^{exp}$ (cm^3 mol^{-1})	$10^2\left(\frac{c_p d}{c_{p,1}^\circ d_1^\circ} - 1\right)$	${}^\phi C_p^{exp}$ ‡ (J K^{-1}mol^{-1})
		$Na_2[H_2EDTA]$			
0.2588		43.681	160.38	−2.262	285.1
0.1631		28.190	158.81	−1.513	261.0
0.1251		21.832	158.14	−1.197	248.0
0.1015		17.826	157.67	−0.988	243.4
0.06069		10.800	156.49	−0.614	225.0
0.03530		6.342	155.48	−0.3668	211.2
0.02597		4.684	155.03	−0.2715	207.4

* m_2 is the stoichiometric (total) molality of EDTA from all species and m_3 is the stoichiometric molality of base.

‡ ${}^\phi Y^{exp}$ used in the heading represents ${}^\phi Y_\Sigma^{exp}$ for solutions containing $[(CH_3)_4N]_4EDTA$, $Na_3[NaEDTA]$, and $K_3[KEDTA]$.

16.3. Because the solutions of present interest contained relatively large amounts of the "extra" electrolyte and also because the electrolytes are of different charge types, two methods were used to carry out these calculations. One method is based on Young's rule and the other is based on Pitzer's ion interaction model.

Young's rule (YOUNG and SMITH, 1954) expresses the apparent molar properties of a mixture of electrolytes in terms of properties (at an ionic strength equal to the total ionic strength of the solution) of the solute components comprising the mixture. Young's rule can be expressed as

$$^{\phi}Y_{\Sigma} = \sum_i \frac{m_i}{\sum_i m_i} {}^{\phi}Y_i + \delta \tag{16.6}$$

where m_i is the molality of the i'th solute, ${}^{\phi}Y_i$ is the corresponding apparent molar property, and δ is an excess mixing term. For solutions containing two solutes whose molalities are denoted by m_2 and m_3, δ has the form

$$\delta = k_{23} \frac{m_2 m_3}{(m_2 + m_3)^2} I = k_{23} F_2 F_3 I \tag{16.7}$$

in which k_{23} is a binary interaction coefficient, $F_i = m_i / \sum m_i$, and I is the total molal ionic strength. Equations 16.6 and 16.7 can also be applied to systems in which one of the solutes dissociates or complexes to form other species. In such cases m_i refers to the molality of each species rather than to the stoichiometric molality of each component.

Apparent molar properties of strong electrolytes can be represented to moderate concentrations by Debye-Hückel equations of the type

$$^{\phi}Y = \bar{Y}^{\circ} + A_Y \omega I^{1/2} + B_Y I + C_Y I^{3/2} \tag{16.8}$$

in which $\bar{Y}_2^{\circ}$ is the value of ${}^{\phi}Y$ at infinite dilution, A_Y is derived from the Debye-Hückel theory (BRADLEY and PITZER, 1979; ANANTHASWAMY and ATKINSON, 1984), and B_Y and C_Y are adjustable parameters. The ionic strength I and the "valence factor" ω are defined and related by

$$I = \frac{1}{2} \sum_i m_i z_i^2 = \omega m \tag{16.9}$$

Calorimetric and densimetric measurements have been made that lead to apparent molar heat capacities and volumes of solutions of $(CH_3)_4NOH$ prepared with

material from Alfa and from Fisher and these results are reported in Chapter 2 for the results obtained for the solutions from Alfa. Apparent molar volumes for the solutions from Fisher are in good agreement with those for the solutions from Alfa, with both of the infinite dilution values showing good agreement with the value calculated from properties of aqueous $(CH_3)_4Cl$, NaCl, and NaOH. The apparent molar heat capacity at infinite dilution derived from the measurements on solutions from Alfa is also in good agreement with the value that can be calculated from heat capacities for the other electrolytes mentioned above. The result from the Fisher salt differs from this value by 11 J $K^{-1}mol^{-1}$. As a result, the data obtained from measurements on solutions from Alfa were weighted more heavily than those obtained for solutions from Fisher.

The results of least squares fits of eq. 16.8 to heat capacities and volumes of solutions of $(CH_3)_4NOH$ and other "auxiliary" electrolytes are reported in Table 16.2. The parameters in Table 16.2 have been used along with the experimental results (Table 16.1) in fitting eqs. 16.6-16.8 to obtain the desired standard state properties of $EDTA^{4-}$(aq) and other parameters as listed in Table 16.3. Results of different fits (different parameters set equal to zero) are mostly in good agreement. Uncertainties in the desired values of $\bar{C}_p^\circ$ are larger than for most of our other investigations because the solutions contained relatively large amounts of the auxiliary electrolyte and also because of the uncertainty in the product ωA_J for highly charged electrolytes such as $[(CH_3)_4N]_4EDTA$. The results of fits with Young's rule as presented in this section, and with the Pitzer model which follows, are plotted in Figures 16.2 and 16.3. These plots illustrate some of the model dependency of the fitted results as well as some of the uncertainties in the experimental data. Estimates of *total* uncertainties (chemical, measurements, Debye- Hückel slopes, and fitting model) in $\bar{V}^\circ$ and $\bar{C}_p^\circ$ for $EDTA^{4-}$(aq) are $\pm$ 2 cm^3mol^{-1} and $\pm$ 25 J $K^{-1}mol^{-1}$, respectively.

16.3.2 Na_3[NaEDTA] and K_3[KEDTA]

Results of measurements on solutions labelled Na_3[NaEDTA] and K_3[KEDTA] are listed in Table 16.1, with experimental quantities and compositions defined as previously specified. Analysis of these results to obtain the desired standard state

Table 16.2: Debye-Hückel parameters for aqueous hydroxides and chlorides at 25.0°C according to eq. 16.8.*

Solute	$\bar{V}^\circ$ ($cm^3 mol^{-1}$)	A_V ($cm^3 kg^{1/2} mol^{-3/2}$)	B_V ($cm^3 kg\ mol^{-2}$)	C_V ($cm^3 kg^{3/2} mol^{-5/2}$)	D_V ($cm^3 kg^2 mol^{-3}$)
$(CH_3)_4NOH$(Fish.)	85.01 ± 0.04	1.8743	−1.483		
$(CH_3)_4NOH$(Alfa)	85.54 ± 0.03	1.8743	−1.609		
NaOH	-5.259 ± 0.019	1.865	1.492	−0.3846	0.03241
KOH	4.917 ± 0.011	1.865	1.224	−0.3033	0.01976
$(CH_3)_4NCl$	107.27 ± 0.03	1.865	−1.33		
NaCl	16.616 ± 0.005	1.865	−0.178	0.179	
KCl	26.89 ± 0.01	1.865	0.0476		

Solute	$\bar{C}_p^\circ$ ($J\ K^{-1} mol^{-1}$)	A_J ($J\ kg^{1/2} K^{-1} mol^{-3/2}$)	B_J ($J\ kg\ K^{-1} mol^{-2}$)	C_J ($J\ kg^{3/2} K^{-1} mol^{-5/2}$)	D_J ($J\ kg^2 K^{-1} mol^{-3}$)	E_J ($J\ kg^{5/2} K^{-1} mol^{-7/2}$)
$(CH_3)_4NOH$(Fish.)	80.9 ± 0.5	32.783	4.897			
$(CH_3)_4NOH$(Alfa)	92.1 ± 0.5	32.783	−1.098			
NaOH	-97.40 ± 0.30	28.95	45.92	−17.78	1.879	
KOH	-130.52 ± 0.22	28.95	32.93	−16.57	3.470	−0.2882
$(CH_3)_4NCl$	107.7 ± 0.2	28.945	−5.0			
NaCl	-84.4 ± 0.2	28.945	15.6	0.179		
KCl	-114.2 ± 0.2	28.945	8.2			

* The values in this table have come directly from DESNOYERS *et al.* (1976), Chapter 2, ROUX *et al.* (1984), PERRON and DESNOYERS (1972), PERRON *et al.* (1976), and FORTIER *et al.* (1974) except for the volumetric values of NaCl and KCl that were obtained by refitting to the data in PICKER *et al.* (1974) and FORTIER *et al.* (1974).

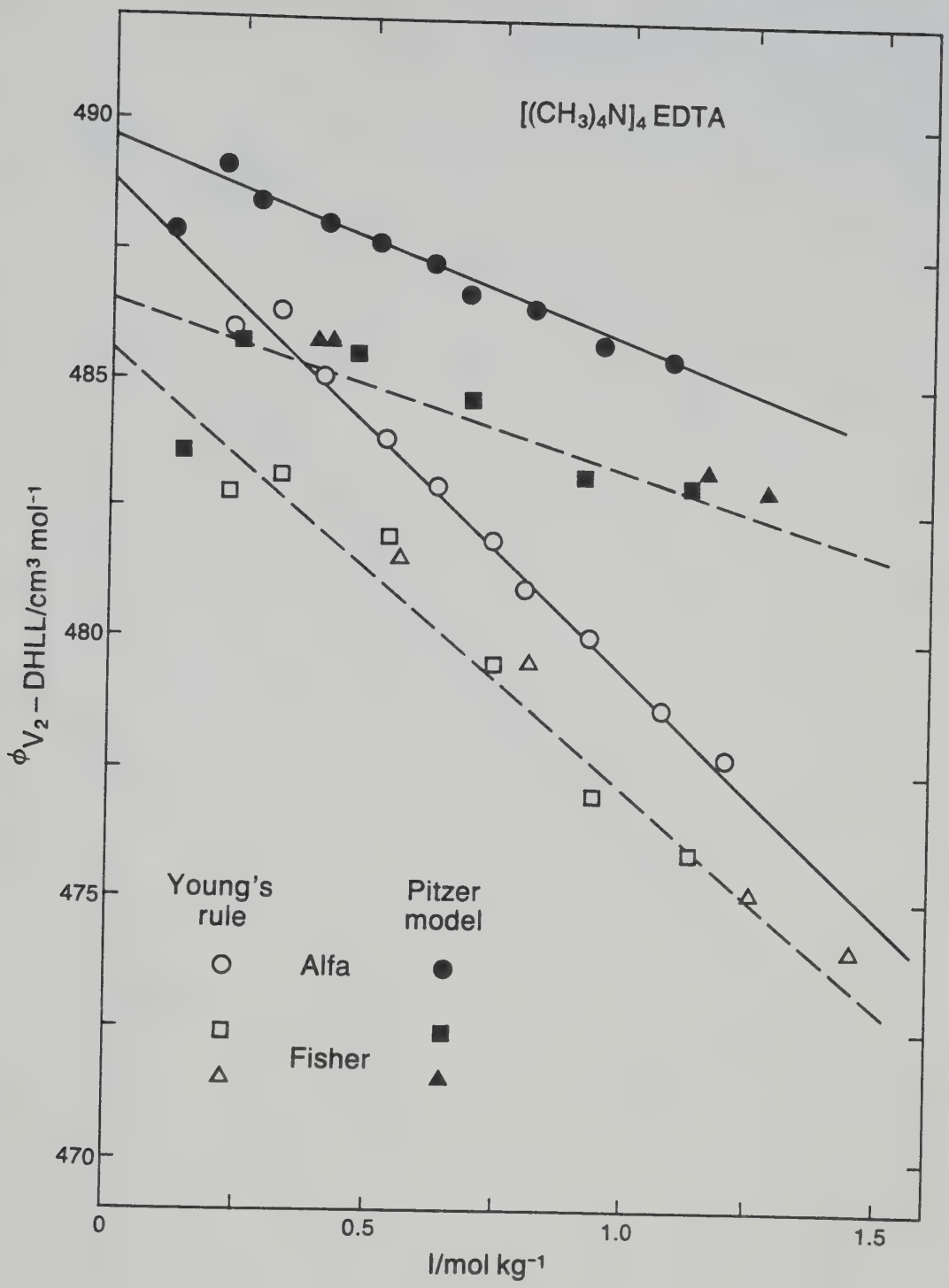

Figure 16.2: Apparent molar volumes for $[(CH_3)_4N]_4EDTA$ minus the Debye- Hückel limiting law (DHLL) contribution against ionic strength as calculated from both Young's rule and the Pitzer model. The selected fits to the Pitzer model were mathematically manipulated to produce linear fits with ionic strength and subsequently do not represent true ionic strength values but rather ωm_2, but do show the desired "goodness" of fit.

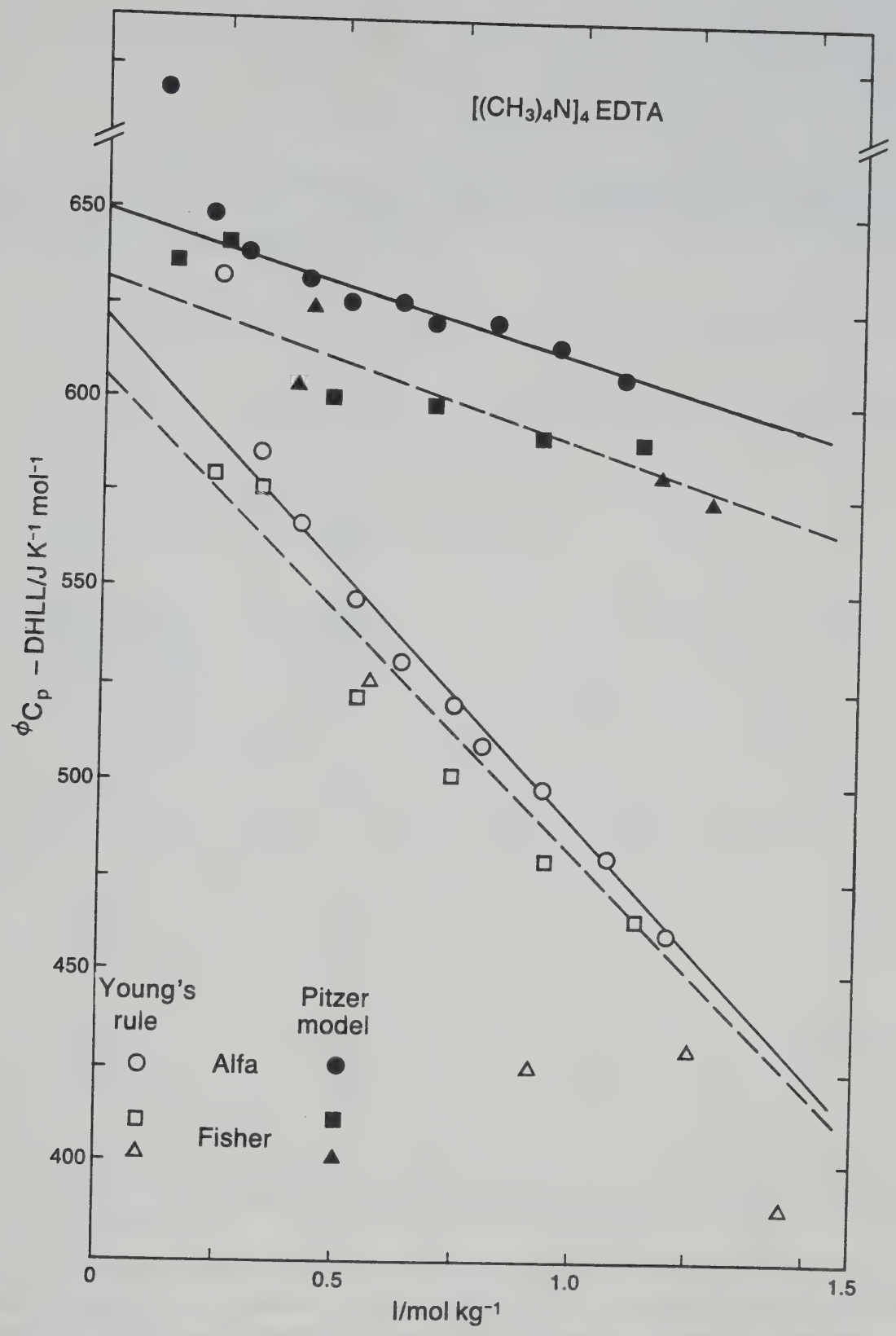

Figure 16.3: Apparent molar heat capacities for $[(CH_3)_4N]_4EDTA$ minus the Debye-Hückel limiting law (DHLL) contribution against ionic strength as calculated from both Young's rule and the Pitzer model. The plotted ionic strength values from the two models are different (see Figure 16.2 caption).

Table 16.3: Conventional standard state (infinite dilution) partial molar volumes, heat capacities, B_V, C_V, and k_{23} parameters for solutions of $[(CH_3)_4N]_4EDTA$ + $(CH_3)_4NOH$ derived using Young's rule.*†

Solute	$\bar{V}^\circ$ ($cm^3 mol^{-1}$)	B_V ($cm^3 kg\ mol^{-2}$)	C_V ($cm^3 kg^{3/2} mol^{-5/2}$)	k_{23}^V ($cm^3 kg\ mol^{-2}$)
Fisher	485.4 ± 0.5	-8.544		1.295
	§485.5 ± 0.7	-8.332		
Alfa	490.2 ± 0.9	-7.108		-6.6
	§488.8 ± 0.3	-9.380		
	490.2 ± 0.8	-14.72	3.9	

Solute	$\bar{C}_p^\circ$ ($J\ K^{-1} mol^{-1}$)	B_J ($J\ kg\ K^{-1} mol^{-2}$)	C_J ($J\ kg^{3/2} K^{-1} mol^{-5/2}$)	k_{23}^J ($J\ kg\ K^{-1} mol^{-2}$)
Fisher	§604 ± 5	-122		-43.2
	605 ± 14	-133		
Alfa	631 ± 5	-118.2		(-43.2)‡
	§622 ± 6	-133.1		
	657 ± 18	-275	104	

* The ± values listed correspond to the statistical estimates of the uncertainties from the least squares fits.

§Values of the parameters $\bar{V}^\circ$ and $\bar{C}_p^\circ$ depend on the fitting equation that is used. The values marked §were adopted as the "best" values from that series of solutions. Based on the differences between fits and other factors discussed in the text, total uncertainties are ± 2 $cm^3 mol^{-1}$ and ± 25 $J\ K^{-1} mol^{-1}$ for $\bar{V}^\circ$ and $\bar{C}_p^\circ$, respectively.

‡k_{23}^J was assumed to be the same as that for the Fisher solutions, which had wider variations in m_2 and m_3.

properties of $NaEDTA^{3-}(aq)$ and $KEDTA^{3-}(aq)$ requires consideration of mixed electrolyte effects as in the previous section. It is also necessary to consider detailed speciation and contributions of "chemical relaxation" to the measured heat capacities. Calculations with the stability constants from DANIELE *et al.* (1985) show that complexes of type $MEDTA^{3-}(aq)$ are the principal species, but concentrations of $EDTA^{4-}(aq)$ are too large to be ignored.

Concentrations of the various species have been obtained with equilibrium constants from DANIELE *et al.* (1985) by way of calculations based on eq. 16.10 as follows:

$$\begin{array}{ccccc} MEDTA^{3-}(aq) & = & M+(aq) & + & EDTA^{4-}(aq) \\ (1-\alpha)m_2 & & (3+\alpha)m_2+m_3 & & \alpha m_2 \end{array} \qquad (16.10)$$

The equilibrium properties of EDTA species have usually been based on a standard state having an ionic strength equal to 0.1 molar rather than the usual infinite dilution reference state. We denote the 0.1 molar reference state by the superscript † instead of ° for the infinite dilution state.

Results obtained by DANIELE *et al.* (1985) for ionic strengths from 0.02 to 1.0 molar have been summarized by the equation

$$\begin{aligned} \log K(I) &= \log K^{\dagger} - z\left[\frac{I^{1/2}}{2+3I^{1/2}} - \frac{0.1^{1/2}}{2+3(0.1)^{1/2}}\right] + \\ &\quad C(I-0.1) + D\left[I^{3/2} - (0.1)^{3/2}\right] \end{aligned} \qquad (16.11)$$

Values of $\log K^{\dagger}$, z, C, and D are listed in Table 16.4 to allow easy calculation of the equilibrium constants. Note that the small numerical differences between molality and molarity are less than the uncertainties in $K(I)$. Results of these speciation calculations are summarized in Table 16.5. The measured apparent molar heat capacities have been corrected for the contributions from chemical relaxation as detailed in Appendix A. Expressions of the type given by eqs. 16.6,16.8 were fitted to the data from ROUX *et al.* (1984) for NaOH and KOH, and calculated values for the hypothetical Na_4EDTA and K_4EDTA species obtained from $[(CH_3)_4N]_4EDTA$ data listed in Table 16.3. These calculations have also made use of auxiliary data for $(CH_3)_4NCl$, NaCl, and KCl (PICKER *et al.*, 1974; DESNOYERS *et al.*, 1976; PERRON and DESNOYERS, 1972; PERRON *et al.*, 1976; FORTIER *et al.*, 1974) listed in Table

16.2, along with eq. 16.7 extended to three electrolytes as in

$$\delta = k_{23}F_2F_3I + k_{24}F_2F_4I + k_{34}F_3F_4I \tag{16.12}$$

to obtain standard state and other parameters. The relative concentrations of the species in the solutions containing $NaEDTA^{3-}(aq)$ allow interactions of the uncomplexed $EDTA^{4-}(aq)$ anion to be ignored, which simplifies eq. 16.12 to eq. 16.7 in this case. On the other hand, analysis of the experimental data for solutions in which $KEDTA^{3-}(aq)$ was an important anion is more complicated because of the larger number of non-negligible parameters to be included in the fit. Results of all of these calculations for solutions containing $NaEDTA^{3-}(aq)$ and $KEDTA^{3-}(aq)$ are given in Table 16.6. The resultant fits and original data for these solutions are plotted in Figures 16.3 and 16.4. These plots show fits to Young's rule as described here and the Pitzer ion interaction model, which follows directly below.

The basic equation in the Pitzer treatment considers the excess free energy to result from long range electrostatic interactions (given by Debye- Hückel theory) and short range binary and ternary interactions. The model yields the following general equation for a mixture of any number of electrolytes (PITZER, 1979, 1984; PHUTELA and PITZER, 1986)

$$\begin{aligned}\frac{G^{EX}}{RT} &= f(I) + 2\sum_c\sum_a m_c m_a (B_{ca} + EC_{ca}) + \\ &\sum_c\sum_{c'} m_c m_{c'}\left(\theta_{cc'} + \sum_a \frac{m_a\psi_{cc'a}}{2}\right) + \sum_a\sum_{a'} m_a m_{a'}\left(\theta_{aa'} + \sum_c \frac{m_c\psi_{caa'}}{2}\right)\end{aligned} \tag{16.13}$$

Here c and a refer to individual cationic and anionic species, $f(I)$ is the Pitzer form of the extended Debye-Hückel equation

$$f(I) = -A_\phi\left(\frac{4I}{1.2}\right)\ln(1 + 1.2I^{1/2}) \tag{16.14}$$

and E is given by

$$E = \sum m_c z_c \tag{16.15}$$

Combination and rearrangement of the equations for the experimental apparent molar properties and appropriate differentiation of equation 16.13 leads to the "Pitzer expressions" that were applied to results for solutions of $[(CH_3)_4N]_4EDTA$

Table 16.4: Equilibrium constant data for $Na^+(aq)$ and $K^+(aq)$ complexation with $EDTA^{4-}(aq)$, from DANIELE *et al.* (1985), for use in eq. 16.11.

	$M^+ + EDTA^{4-} = MEDTA^{3-}$		$nH^+ + EDTA^{4-} = H_nEDTA^{n-4}$		
Property	Na^+	K^+	$n = 1$	$n = 2$	$n = 3$
$\log K^\dagger$	1.81	0.80	10.39	16.58	19.26
z	8	8	8	14	18
C	1.84	1.84	1.84	3.27	4.3
D	−0.96	−0.96	−0.96	−1.68	−2.2

Table 16.5: Concentrations of species in solutions containing Na_3[NaEDTA] + NaOH and K_3[KEDTA] + KOH.*

m_2 (mol kg^{-1})	m_3 (mol kg^{-1})	α	$(1-\alpha)m_2$ (mol kg^{-1})	αm_2 (mol kg^{-1})	I (mol kg^{-1})	${}^{\phi}C_{p,\Sigma}^{rel}$ (J K^{-1}mol^{-1})	${}^{\phi}C_{p,\Sigma}$ (J K^{-1}mol^{-1})
			Na_3[NaEDTA] + NaOH				
0.2057	0.1609	0.01884	0.2018	0.00387	1.4106	0.89	161.4
0.1744	0.1566	0.02106	0.1707	0.00367	1.2176	0.94	138.3
0.1552	0.1516	0.02317	0.1539	0.00360	1.0993	0.98	122.5
0.1321	0.1507	0.02671	0.1286	0.00353	0.9577	1.05	102.2
0.1168	0.1486	0.02989	0.1133	0.00349	0.8636	1.10	87.58
0.09857	0.1461	0.03482	0.09513	0.00343	0.7512	1.16	68.65
0.07562	0.1429	0.04348	0.07233	0.00329	0.6098	1.24	41.01
0.05594	0.1402	0.05403	0.05291	0.00302	0.4879	1.25	15.88
0.03969	0.1380	0.06578	0.03708	0.00261	0.3865	1.18	−7.00
0.02053	0.1353	0.08411	0.01880	0.00173	0.2654	0.87	−40.76
			K_3[KEDTA] + KOH				
0.2049	0.1763	0.1713	0.1698	0.03510	1.5460		37.04
0.1456	0.1669	0.2031	0.1160	0.02957	1.1587		2.027
0.1237	0.1635	0.2255	0.09581	0.02790	1.0173		−13.20
0.08943	0.1580	0.2778	0.06459	0.02484	0.7940		−37.47
0.05981	0.1533	0.3460	0.03911	0.02070	0.5950		−61.2
0.03655	0.1497	0.4194	0.02122	0.01533	0.4303		−82.7
0.01932	0.1469	0.4846	0.00996	0.00936	0.3003		−99.4
0.1740	0.2763	0.1667	0.1450	0.02901	1.4365		−9.87
0.1641	0.3423	0.1611	0.1377	0.02645	1.4329		−5.96
0.01746	0.2302	0.4098	0.01302	0.00715	0.3636		−98.3
0.01577	0.3046	0.3574	0.01013	0.00563	0.4218		−98.0

* m_2 is the stoichiometric molality of M_3[MEDTA] and ${}^{\phi}C_{p,\Sigma} = {}^{\phi}C_{p,\Sigma}^{exp}$ - ${}^{\phi}C_{p,\Sigma}^{rel}$.

Table 16.6: Standard state (infinite dilution) partial molar volumes, heat capacities, B_Y, C_Y and k_{23} parameters for solutions of Na_3[NaEDTA] + NaOH and K_3[KEDTA] + KOH from Young's rule.*

Solute	$\bar{V}^\circ$ ($cm^3 mol^{-1}$)	B_V ($cm^3 kg\ mol^{-2}$)	C_V ($cm^3 kg^{3/2} mol^{-5/2}$)	k_{23}^V ($cm^3 kg\ mol^{-2}$)
Na_3[NaEDTA]	§142.6 ± 0.1	−1.061		
	141.8 ± 0.6	−2.191		3.88
K_3[KEDTA]‡	176.1 ± 0.4	0.916		

Solute	$\bar{C}_p^\circ$ ($J\ K^{-1} mol^{-1}$)	B_J ($J\ kg\ K^{-1} mol^{-2}$)	C_J ($J\ kg^{3/2} K^{-1} mol^{-5/2}$)	k_{23}^J ($J\ kg\ K^{-1} mol^{-2}$)
Na_3[NaEDTA]	79.4 ± 2	−3.06		
	90.3 ± 5	−41.2	26.3	
	§98.9 ± 8	22.8		−88.5
K_3[KEDTA]‡	−79.8 ± 4	−10.35		

* The ± values listed correspond to the statistical estimates of the uncertainties from the least squares fits.

§Values of the parameters $\bar{V}^\circ$ and $\bar{C}_p^\circ$ depend on the fitting equation that is used. The values marked §were adopted as the "best" values from that series of solutions. Based on the differences between fits and other factors discussed in the text, total uncertainties are about ± 2 $cm^3 mol^{-1}$ and ± 25 $J\ K^{-1} mol^{-1}$ for $\bar{V}^\circ$ and $\bar{C}_p^\circ$, respectively.

‡In obtaining the values listed, data for solutions with KOH concentrations greater than 0.2 molal were not included in the fits.

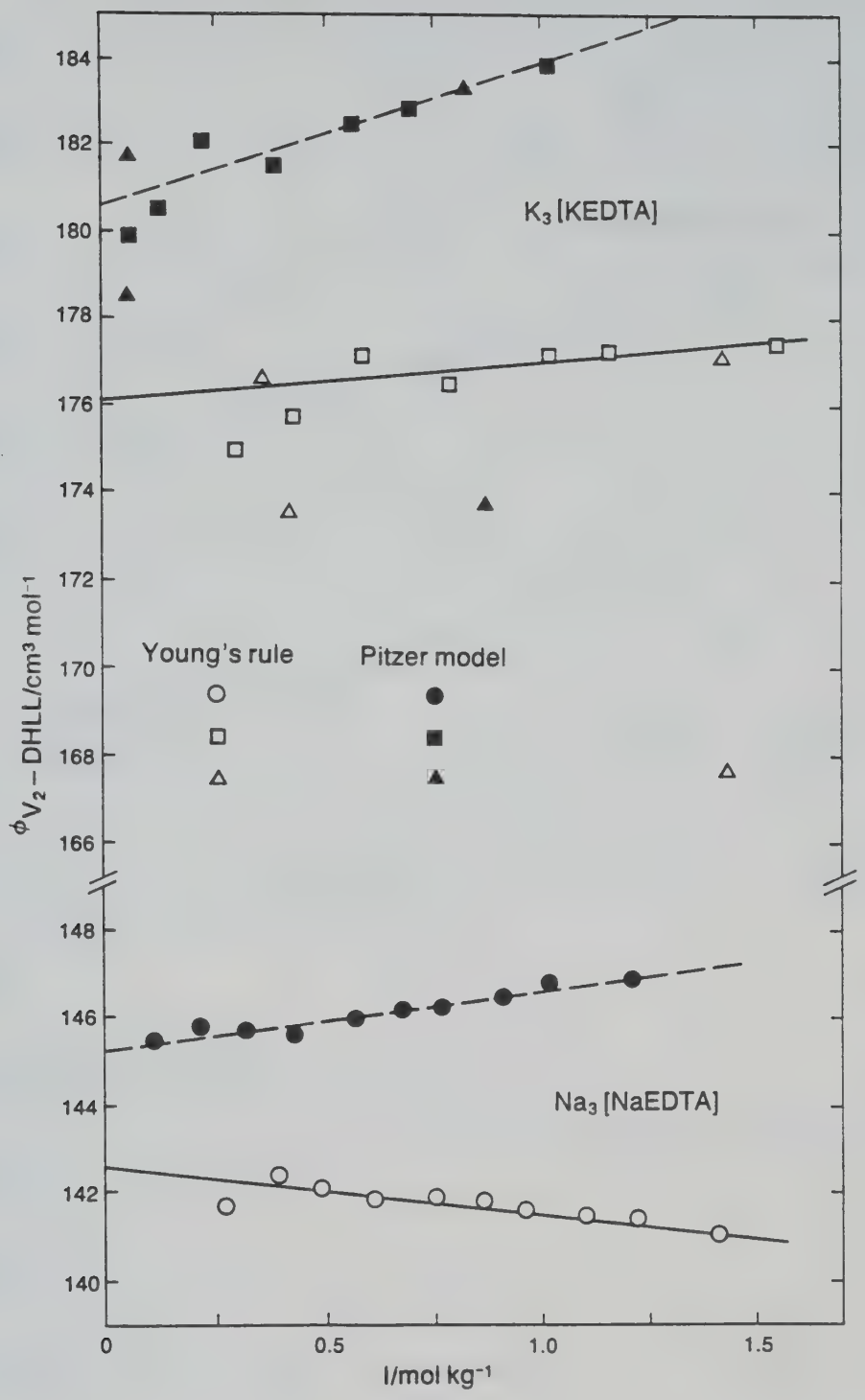

Figure 16.4: Apparent molar volumes for Na_3[NaEDTA] and K_3[KEDTA] minus the Debye-Hückel limiting law (DHLL) contribution against ionic strength as calculated from both Young's rule and the Pitzer model. The plotted ionic strengths from the two models are different (see Figure 16.2 caption). Δ represent higher OH^- / $KEDTA^{3-}$ ratios.

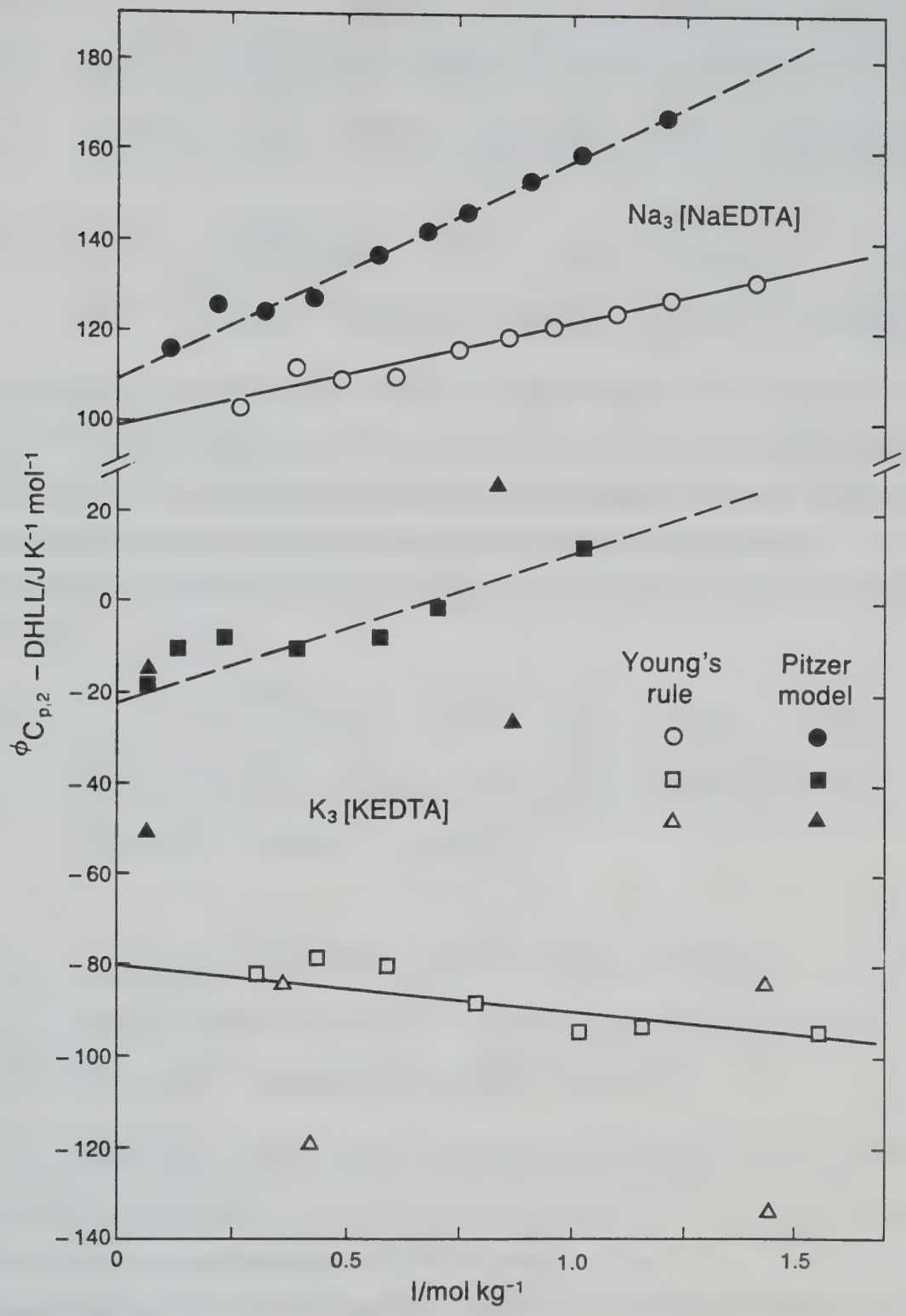

Figure 16.5: Apparent molar heat capacities for Na_3[NaEDTA] and K_3[KEDTA] minus the Debye-Hückel limiting law (DHLL) contribution against ionic strength as calculated from both Young's rule and the Pitzer model. The plotted ionic strengths from the two models are different (see Fig. 16.2 caption). Δ represent higher OH^- - $KEDTA^{3-}$ ratios.

+ $(CH_3)_4NOH$:

$$^{\phi}V_{\Sigma} = \frac{1}{m_2+m_3}\left[\left(\frac{A_V I}{1.2}\right)\ln(1+1.2I^{1/2}) + m_2\bar{V}_2^{\circ} + m_3V_3^{\circ} + 2RT\left(m_c m_2 B_2^V + m_c^2 m_2 C_2^V + m_c m_3 B_3^V + m_c^2 m_3 C_3^V + m_2 m_3 \theta_{23}^V\right)\right] \quad (16.16)$$

$$^{\phi}C_{p,\Sigma} = \frac{1}{m_2+m_3}\left[\left(\frac{A_J I}{1.2}\right)\ln(1+1.2I^{1/2}) + m_2\bar{C}_{p,2}^{\circ} + m_3C_{p,3}^{\circ} - 2RT^2\left(m_c m_2 B_2^J + m_c^2 m_2 C_2^J + m_c m_3 B_3^J + m_c^2 m_3 C_3^J + m_2 m_3 \theta_{23}^J\right)\right] \quad (16.17)$$

In these equations m_c refers to the molality of the common cation, given by $m_c = 4m_2+m_3$. The contributions of non-ideal ternary interactions to the excess properties have been neglected because previous experience has suggested that such interactions are unimportant in the relatively dilute solutions under consideration.

Similar more complicated expressions that are applicable to solutions of MOH + M_3[MEDTA] are as follows:

$$^{\phi}V_{\Sigma} = \frac{1}{m_2+m_3}\left[\left(\frac{A_V I}{1.2}\right)\ln(1+1.2I^{1/2}) + m_2\bar{V}_2^{\circ} + m_3V_3^{\circ} + m_4V_4^{\circ} + 2RT\left(m_c m_2 B_2^V + m_c^2 m_2 C_2^V + m_c m_3 B_3^V + m_c^2 m_3 C_3^V + m_c m_4 B_4^V + m_2 m_3 \theta_{23}^V + m_2 m_4 \theta_{24}^V + m_3 m_4 \theta_{34}^V\right)\right] \quad (16.18)$$

$$^{\phi}C_{p,\Sigma} = \frac{1}{m_2+m_3}\left[\left(\frac{A_V I}{1.2}\right)\ln(1+1.2I^{1/2}) + m_2\bar{C}_{p,2}^{\circ} + m_3C_{p,3}^{\circ} + m_4C_{p,4}^{\circ} - 2RT^2\left(m_c m_2 B_2^J + m_c^2 m_2 C_2^J + m_c m_3 B_3^J + m_c^2 m_3 C_3^J + m_c m_4 B_4^J + m_2 m_3 \theta_{23}^J + m_2 m_4 \theta_{24}^J + m_3 m_4 \theta_{34}^J\right)\right] \quad (16.19)$$

For systems in which one of the solute components dissociates, m_2, m_3, and m_4 all refer to equilibrium molalities of different species rather than to the stoichiometric molalities as is the case elsewhere in this Chapter.

This application of the Pitzer model to solutions of a single electrolyte $M_{\nu_M}X_{\nu_X}$ leads (PITZER *et al.*, 1984) to

$$^{\phi}V = \bar{V}^{\circ} + \nu \mid z_M z_X \mid \left(\frac{A_V}{2b}\right)\ln(1+bI^{1/2}) + 2\nu_M\nu_X RT\left[mB^V + m^2(\nu_M z_M)C^V\right] \quad (16.20)$$

and

$$^{\phi}C_p = \bar{C}_p^{\circ} + \nu \mid z_M z_X \mid \left(\frac{A_J}{2b}\right) \ln(1 + bI^{1/2}) - 2\nu_M \nu_X RT^2 \left[mB^J + m^2(\nu_M z_M)C^J\right] \tag{16.21}$$

in which $\nu = \nu_M + \nu_X$, $b = 1.2$, C_Y is an adjustable parameter, and B_Y is a function of ionic strength that has the form

$$B_Y = \beta^{(0)Y} + \frac{2\beta^{(1)Y}\left[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})\right]}{\alpha^2 I} \tag{16.22}$$

Here $\beta^{(0)Y}$ and $\beta^{(1)Y}$ are adjustable parameters and $\alpha = 2$.

Equations of type 16.16-16.22 were fitted to the experimental data for mixed electrolytes as listed in Table 16.1 (with auxiliary data from Tables 16.5 and 16.7) to obtain the desired parameters that are listed in Table 16.8. Plots of fits to these data are given in Figures 16.2-16.5.

16.3.3 $[(CH_3)_4N]_3HEDTA$ and Na_2H_2EDTA

The experimental results for solutions of Na_2H_2EDTA and $[(CH_3)_4N]_3HEDTA$ are expressed as experimental apparent molar properties ($^{\phi}V^{exp}$, $^{\phi}C_p^{exp}$) defined by

$$^{\phi}Y = \frac{Y_{sol} - n_1 Y_1^{\circ}}{n_2} \tag{16.23}$$

in which meanings of symbols have been specified previously. These experimental results are listed in Table 16.1.

The important equilibria in solutions of $[(CH_3)_4N]_3HEDTA$ are

$$\begin{array}{ccccccc} HEDTA^{3-}(aq) & + & H_2O(l) & = & H_2EDTA^{2-}(aq) & + & OH^-(aq) \\ (1-\alpha-\beta)m_2 & & \alpha m_2 & & \alpha m_2 & & (\alpha-\beta)m_2 \end{array} \tag{16.24}$$

and

$$\begin{array}{ccccccc} HEDTA^{3-}(aq) & + & OH^-(aq) & = & EDTA^{4-}(aq) & + & H_2O(l) \\ (1-\alpha-\beta)m_2 & & (\alpha-\beta)m_2 & & \beta m_2 & & \end{array} \tag{16.25}$$

The experimental apparent molar heat capacities and volumes contain contributions from the $H_2EDTA^{2-}(aq)$ and $EDTA^{4-}(aq)$ anions as well as the $HEDTA^{3-}(aq)$ anion

Table 16.7: Values of parameters from the Pitzer model for aqueous hydroxides and chlorides.*

Solute	$\bar{V}^\circ$ ($cm^3 mol^{-1}$)	$10^4\beta^{(0)V}$ ($cm^3 kg\ J^{-1} mol^{-1}$)	$10^4\beta^{(1)V}$ ($cm^3 kg\ J^{-1} mol^{-1}$)	$10^5 C^V$ ($cm^3 kg^2 J^{-1} mol^{-2}$)
$(CH_3)_4NOH$ (Fisher)	85.16 ± 0.06	-2.000		
$(CH_3)_4NOH$ (Alfa)	85.64 ± 0.03	-2.179		
NaOH	-5.47 ± 0.06	2.235	6.433	-0.597
KOH	4.77 ± 0.03	1.908	5.806	-0.518
$(CH_3)_4NCl$	107.27 ± 0.01	-1.861	1.578	
NaCl	16.63 ± 0.01	1.155	0.387	
KCl	26.91 ± 0.01	1.288	0.316	

Solute	$\bar{C}_p^\circ$ ($J\ K^{-1} mol^{-1}$)	$10^5\beta^{(0)J}$ ($kg\ mol^{-1} K^{-2}$)	$10^4\beta^{(1)J}$ ($kg\ mol^{-1} K^{-2}$)	$10^6 C^J$ ($kg^2 mol^{-2} K^{-2}$)
$(CH_3)_4NOH$ (Fisher)	80.2 ± 1	-0.684	-0.154	
$(CH_3)_4NOH$ (Alfa)	94.0 ± 1	-0.984	0.120	
NaOH	-101.0 ± 1	-1.307	-0.528	0.630
KOH	-133.5 ± 0.9	-0.806	-0.440	0.248
$(CH_3)_4NCl$	107.2 ± 0.1	-0.1409	-0.02144	
NaCl	-84.9 ± 0.1	-1.544	-0.0174	
KCl	-114.7 ± 0.1	-1.024	-0.0237	

* The $\pm$ values listed here correspond to statistical estimates of the standard deviations of the intercepts. The values in this table were obtained from refitting results from PICKER *et al.* (1974), DESNOYERS *et al.* (1976), Chapter 2, ROUX *et al.* (1984), PERRON and DESNOYERS (1972), PERRON *et al.* (1976), and FORTIER *et al.* (1974).

Table 16.8: Values of parameters from the Pitzer model applied to solutions of $[(CH_3)_4N]_4EDTA$ + $(CH_3)_4NOH$, $Na_3[NaEDTA]$ + NaOH, and $K_3[KEDTA]$ + KOH.*

Solute	$\bar{V}_2^\circ$ (cm^3mol^{-1})	$10^4\beta_2^{(0)V}$ ($cm^3kg\ J^{-1}mol^{-1}$)	$10^4\beta_2^{(1)V}$ ($cm^3kg\ J^{-1}mol^{-1}$)	$10^5\theta_{23}^V$ ($cm^3kg^2J^{-1}mol^{-2}$)
$[(CH_3)_4N]_4EDTA$ (Fisher)	486.5 ± 0.5	-16.09		7.51
$[(CH_3)_4N]_4EDTA$ (Alfa)	489.7 ± 0.3	-19.63		
$Na_3[NaEDTA]$	§145.2 ± 0.1	5.748		
	146.2 ± 0.1	8.239	-1.997	
$K_3[KEDTA]$‡	180.6 ± 0.4	12.90		

Solute	$\bar{C}_p^\circ$ ($J\ K^{-1}mol^{-1}$)	$10^5\beta^{(0)J}$ ($kg\ mol^{-1}K^{-2}$)	$10^4\beta^{(1)J}$ ($kg\ mol^{-1}K^{-2}$)	10^6C^J ($kg^2mol^{-2}K^{-2}$)
$[(CH_3)_4N]_4EDTA$	§$632. \pm 8$	7.070		
(Fisher)	$631. \pm 8$	6.632		0.275
$[(CH_3)_4N]_4EDTA$ (Alfa)	$649. \pm 4$	6.309		
$Na_3[NaEDTA]$	§109.1 ± 1.9	-6.524		
	124.5 ± 13	-7.935	1.108	
$K_3[KEDTA]$‡	-22.8 ± 6	-4.565		

* The ± values listed correspond to the statistical estimates of the uncertainties from the least squares fits.

§Values of the parameters $\bar{V}^\circ$ and $\bar{C}_p^\circ$ depend on the fitting equation that is used. The values marked §were adopted as the "best" values from that series of solutions. Based on the differences between fits and other factors discussed in the text, total uncertainties are about ± 2 cm^3mol^{-1} and ± 25 $J\ K^{-1}mol^{-1}$ for $\bar{V}^\circ$ and $\bar{C}_p^\circ$, respectively.

‡ In obtaining the values listed, solutions with KOH concentrations of less than 0.2 molal were used.

that is the principal species of interest here. The experimental apparent molar heat capacities also contain relaxation contributions associated with the equilibria described by eqs. 16.24 and 16.25. Evaluations of the relaxation contributions are presented in Appendix A.

Concentrations of all species in solutions in which $HEDTA^{3-}(aq)$ was the principal anion have been calculated by way of eqs. 16.24 and 16.25 in combination with equilibrium constants from DANIELE *et al.* (1985) for EDTA equilibria and for the ionization of water from SWEETON *et al.* (1974) with results that are summarized in Table 16.9.

The experimental apparent molar properties of these solutions can be expressed as the sum of the apparent molar properties of the individual species present weighted according to concentrations present (same basic assumption as in Young's rule)

$$\begin{aligned} {}^{\phi}Y^{exp} = {} & (1-\alpha-\beta){}^{\phi}Y\left[3(CH_3)_4N^+ + HEDTA^{3-}\right] + \\ & \alpha\,{}^{\phi}Y\left[2(CH_3)_4N^+ + H_2EDTA^{2-}\right] + \beta\,{}^{\phi}Y\left[4(CH_3)_4N^+ + EDTA^{4-}\right] + \\ & (\alpha-\beta){}^{\phi}Y\left[(CH_3)_4NOH\right] - (\alpha-\beta)Y^{\circ}(H_2O) \end{aligned} \qquad (16.26)$$

The standard state volume and heat capacity for water listed in Table 16.10 was used along with data for $[2(CH_3)_4N^+ + H_2EDTA^{2-}]$ calculated from previously reported properties (HOVEY and TREMAINE, 1985) for Na_2H_2EDTA and properties of the auxiliary electrolytes $(CH_3)_4NCl$ and NaCl as listed in Table 16.2. Equations of type 16.8 and 16.26 have been fitted to the experimental data to obtain the desired information about the apparent molar properties of $[3(CH_3)_4N^+ + HEDTA^{3-}]$ as listed in Table 16.11. Plots of the fitted equation 16.8 to the experimental results are shown in Figures 16.6 and 16.7.

The principal equilibria in solutions containing $H_2EDTA^{2-}(aq)$ as the principal anion are

$$\begin{array}{lcl} H_2EDTA^{2-}(aq) & = & H^+(aq) + HEDTA^{3-}(aq) \\ (1-\alpha-\beta)m_2 & & (\alpha-\beta)m_2 \quad \alpha m_2 \end{array} \qquad (16.27)$$

and

$$\begin{array}{lcl} H_2EDTA^{2-}(aq) + H^+(aq) & = & HEDTA^{3-}(aq) \\ (1-\alpha-\beta)m_2 \quad (\alpha-\beta)m_2 & & \beta m_2 \end{array} \qquad (16.28)$$

Table 16.9: Speciation of solutions of $[(CH_3)_4N]_3HEDTA$ and Na_2H_2EDTA.

m_2 (mol kg^{-1})	$10^2\alpha$	$10^2\beta$	${}^{\phi}C_p^{rel}$ J K^{-1}mol^{-1}	${}^{\phi}C_p^{exp}$ J K^{-1}mol^{-1}
		$[(CH_3)_4N]_3HEDTA$		
0.2194	0.8406	0.8389		705.3
0.1710	0.8286	0.8264		694.2
0.1299	0.8242	0.8214		694.0
0.1078	0.8226	0.8193		687.4
0.08617	0.8220	0.8181		683.2
0.06433	0.8206	0.8157		679.4
0.03648	0.8122	0.8039		673.1
0.01649	0.7908	0.7714		665.5
		Na_2H_2EDTA		
0.2588	1.755	1.741	7.07	278.0
0.1631	1.776	1.752	7.15	253.9
0.1251	1.780	1.748	7.15	240.9
0.1015	1.780	1.740	7.15	233.2
0.06069	1.773	1.708	7.09	214.8
0.03530	1.754	1.652	6.96	201.0
0.02597	1.743	1.614	6.89	197.3

Table 16.10: Selected conventional partial molar properties for aqueous ions at $I = 0$ (superscript $\circ$) and $I = 0.1$ molal (superscript $\dagger$) and for liquid water.*

Ion	$\bar{C}^{\circ}_{p,2}$ (J $K^{-1}mol^{-1}$)	$\bar{C}^{\dagger}_{p,2}$ (J $K^{-1}mol^{-1}$)	$\bar{V}^{\circ}_{2}$ (cm^3mol^{-1})	$\bar{V}^{\dagger}_{2}$ (cm^3mol^{-1})
H^+	0	0	0	0
Na^+	42.8	46.2	−1.21	−1.08
K^+	13.0	14.9	9.00	9.23
$(CH_3)_4N^+$	234.9	234.1	89.38	89.34
Cl^-	−127.2	−113.7	17.89	18.55
ClO_4^-	−25.5	−9.9	43.99	44.64
OH^-	−140.2	−122.0	−4.05	−3.03
$H_2O(l)$	75.291		18.068	
H_2EDTA^{2-}	81.0	129.3	156.3	159.2
$HEDTA^{3-}$	−82.0	−25.2	151.2	154.8
$EDTA^{4-}$	−310	−186	131	138
H_3EDTA^-	(210)	(284)	(159)	(162)
$NaEDTA^{3-}$	−24	58	148	151
$KEDTA^{3-}$	−90	−33	151	154

* The values for the EDTA species were derived from the present work. Values for the other ions were derived from the results listed in Table 16.2, except $Cl^-(aq)$ from ALLRED and WOOLLEY (1981) and $ClO_4^-(aq)$ from Chapter 2. Values for $H_2O(l)$ were taken from WAGMAN *et al.* (1982). Bracketed values represent estimates as described in the text.

Table 16.11: Standard state (infinite dilution) partial molar heat capacities, volumes and B_Y parameters at 25.0°C.*

Solute	${}^{\phi}C^{\circ}_{p,2}$ (J $K^{-1}mol^{-1}$)	B_J (J kg $K^{-1}mol^{-2}$)	C_J (J $kg^{3/2}K^{-1}mol^{-5/2}$)
Na_2H_2EDTA	166.6 ± 0.7	42.19	
$[(CH_3)_4N]_3HEDTA$	622.7 ± 1.6	−238.9	112.2

Solute	${}^{\phi}V^{\circ}_2$ (cm^3mol^{-1})	B_V ($cm^3kg\ mol^{-2}$)	C_V ($cm^3kg^{3/2}mol^{-5/2}$)
Na_2H_2EDTA	153.87 ± 0.11	2.347	
$[(CH_3)_4N]_3HEDTA$	419.3 ± 0.2	−10.69	3.511

* The ± values listed correspond to the statistical estimates of the uncertainties from the least squares fits.

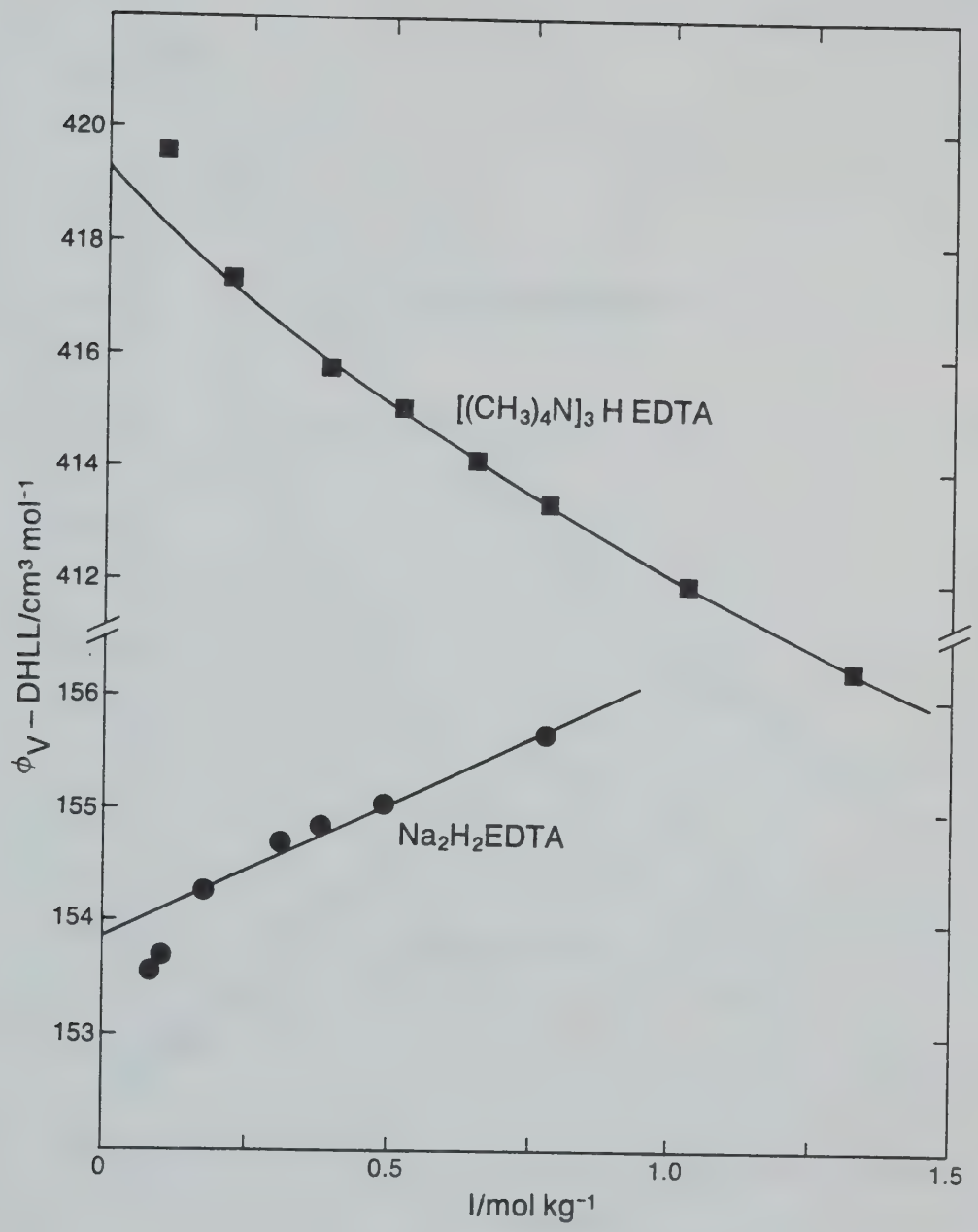

Figure 16.6: Apparent molar volumes for Na_2H_2EDTA and $[(CH_3)_4N]_3HEDTA$ minus the Debye-Hückel limiting law (DHLL) contribution against ionic strength.

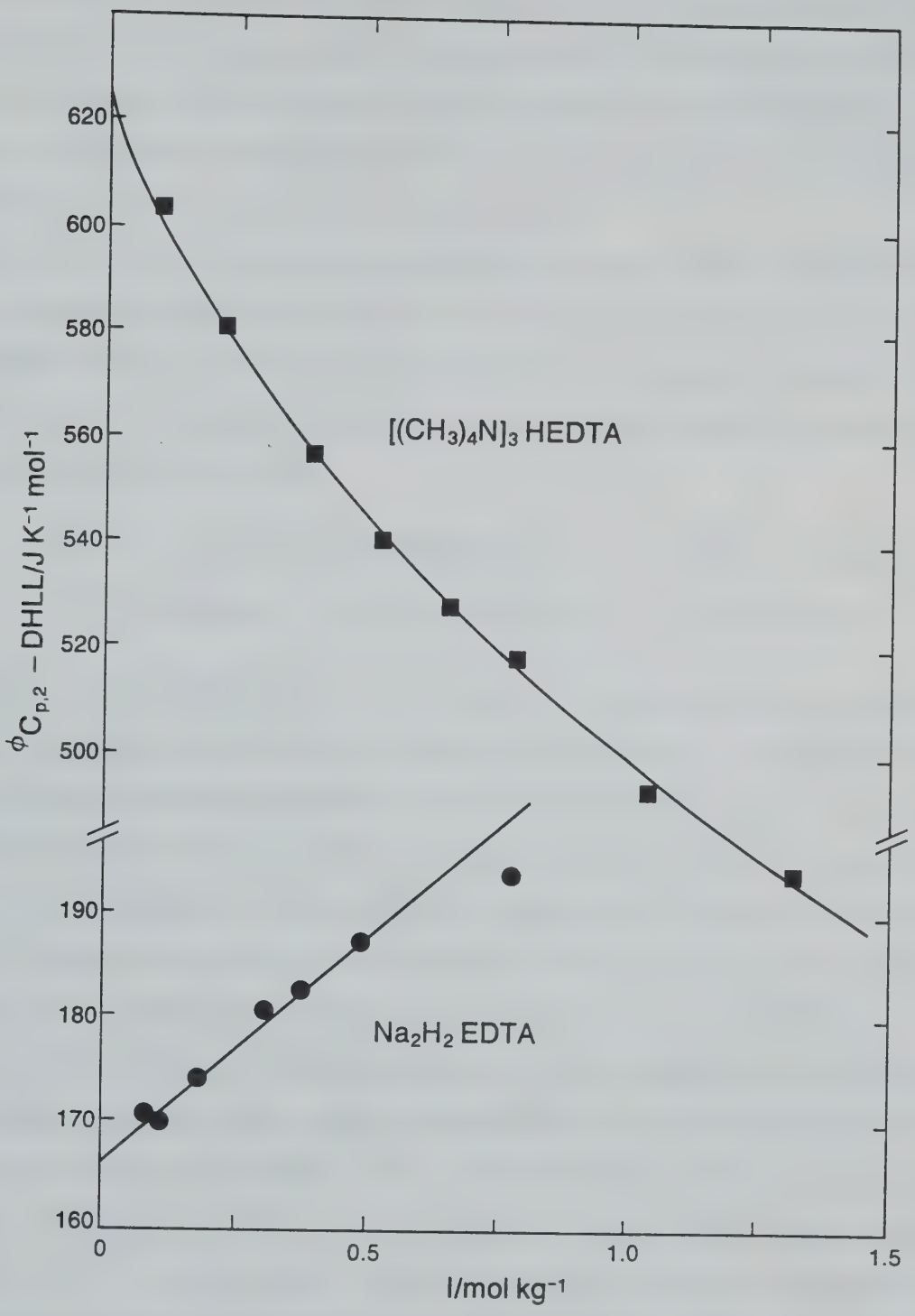

Figure 16.7: Apparent molar heat capacities for Na_2H_2EDTA and $[(CH_3)_4N]_3HEDTA$ minus the Debye-Hückel limiting law (DHLL) contribution against ionic strength.

The experimental apparent molar heat capacities and volumes contain contributions from the $HEDTA^{3-}(aq)$ and $H_3EDTA^-(aq)$ anions as well as $H_2EDTA^{2-}(aq)$ that is of principal interest here, and the apparent molar heat capacities also contain relaxation contributions asscociated with the equilibria represented by eqs. 16.27 and 16.28. Appendix A describes evaluation of these relaxation contributions from equilibrium constants and enthalpies of reaction.

Concentrations of all species in these solutions have been calculated from equilibrium constants given by DANIELE *et al.* (1985) and SWEETON *et al.* (1974) in combination with eqs. 16.27 and 16.28, with results summarized in Table 16.9.

The experimental apparent molar properties are expressed as appropriate sums as done previously in eq. 16.26:

$$\begin{aligned} {}^{\phi}Y^{exp} \;=\; & (1-\alpha-\beta){}^{\phi}Y\left(2Na^+ + H_2EDTA^{2-}\right) + \alpha\,{}^{\phi}Y\left(3Na^+ + HEDTA^{3-}\right) + \\ & \beta\,{}^{\phi}Y\left(H_3EDTA^-\right) + (2\beta-\alpha){}^{\phi}Y\left(Na^+\right) + (\alpha-\beta){}^{\phi}Y\left(H^+\right) \qquad (16.29) \end{aligned}$$

To make use of eq. 16.29 the standard state heat capacity and volume of $Na^+(aq)$ was used as listed in Table 16.10. Properties of $3Na^+(aq)$ + $HEDTA^{3-}(aq)$ have come come from the measurements and calculations based on eq. 16.26. There are two indirect routes to the required properties of $H_3EDTA^-(aq)$. In previous work (HOVEY and TREMAINE, 1985) $d\Delta H/dT$ results (cited later) for the ionization of $H_2EDTA^{2-}(aq)$ were combined with measured heat capacities for $H_2EDTA^{2-}(aq)$ to obtain a value (large uncertainty) for the heat capacity of $H_3EDTA^-(aq)$. Another route is to estimate the desired standard state properties for $H_3EDTA^-(aq)$ on the basis of the now reliably known properties of other EDTA species and trends observed for a few other systems. Plots of the standard state heat capacities and volumes for the known EDTA ions are shown in Figure 16.8. These trends allow estimation of $\bar{V}^\circ \approx 159\ cm^3mol^{-1}$ and $\bar{C}_p^\circ \approx 210\ J\ K^{-1}mol^{-1}$ for $H_3EDTA^-(aq)$. Fortunately, because β values used in eq. 16.29 are small, the uncertainties in these estimated values do not cause much uncertainty in the desired properties of $2Na^+(aq)$ + $H_2EDTA^{2-}(aq)$. Finally, using auxiliary results mentioned here, fits of eqs. 16.8 and 16.29 to the experimental apparent molar properties listed in Table 16.1 have led to the desired properties of $2Na^+(aq)$ + $H_2EDTA^{2-}(aq)$ that are listed in Table 16.11. Figures 16.6 and 16.7 show plots of fits of eq. 16.8 to the experimental data.

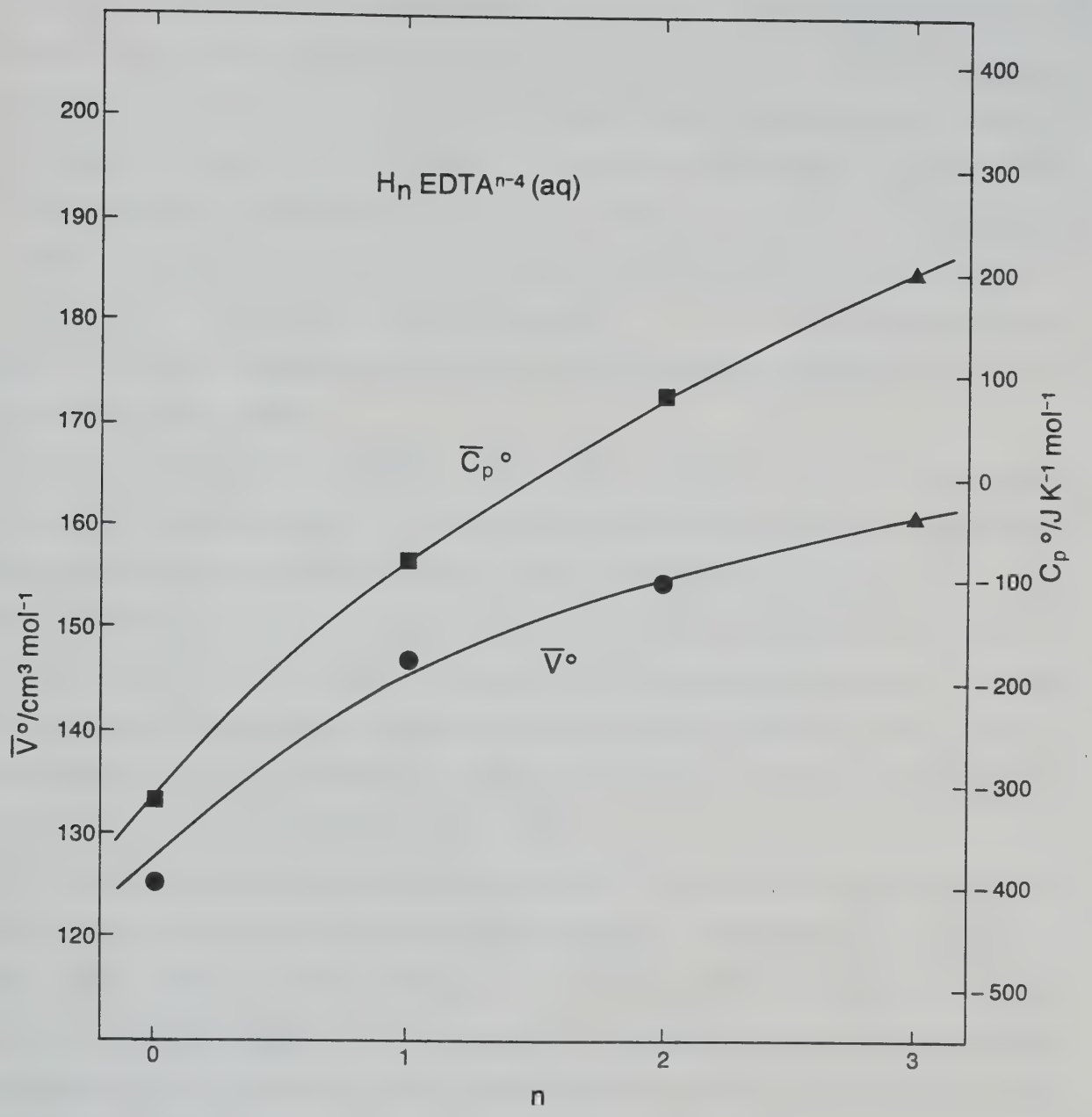

Figure 16.8: Hydrogen ligand number dependence of the limiting partial molar volumes and heat capacities for EDTA ions with 1-3 protons.

16.4 Selections of thermodynamic data at 25°C

Previous selections (HOVEY and TREMAINE, 1985) of "best" equilibrium constants from ANDEREGG (1977) for the ionization reactions of $H_4EDTA(aq)$ at 25°C and 0.1 molar ionic strength have been extended by accepting the equilibrium constants reported by DANIELE *et al.* (1985). The equilibrium constant data for the two protonation reactions of $H_4EDTA(aq)$ are much less certain than the other values. The value listed by ANDEREGG (1977) was chosen for the first protonation step of H_4EDTA and also the recommendations of ANDEREGG (1977) and VASIL'EV *et al.* (1979) were considered in estimating $\log K^{\dagger} = -1.2 \pm 0.6$ for protonation of $H_5EDTA^+(aq)$, by considering the trends in all of the other equilibrium constants of $H_4EDTA(aq)$ at 0.1 molar.

Several investigations (DANIELE *et al.*, 1985; ANDEREGG, 1977; SCHWARZENBACH and ACKERMANN, 1947; WATTERS and SCHUPP, 1968; PALATY, 1963; BOTTS *et al.*, 1965; CARR and SWARTZFAGER, 1973; ANDEREGG, 1967) have led to values of the equilibrium constant for association of $Na^+(aq)$ with $EDTA^{4-}(aq)$; here the results of DANIELE *et al.* (1985) were selected. The chosen equilibrium constants for association of $K^+(aq)$ with $EDTA^{4-}(aq)$ reported by DANIELE *et al.* (1985) are in good agreement with results from others (WATTERS and SCHUPP, 1968; BOTTS *et al.*, 1965; CARR and SWARTZFAGER, 1973).

Some previously selected choices (HOVEY and TREMAINE, 1985) for ΔH values for the ionization of $H_4EDTA(aq)$ have been revised. Averaged direct calorimetric values [many cited by CHRISTENSEN *et al.* (1975)] obtained usually at 0.1 molar (some values were adjusted to 0.1 molar from equations given by the respective authors) and 25°C (VASIL'EV *et al.*, 1973, 1974, 1976, 1977a,b, 1978, 1979; CHRISTENSEN *et al.*, 1969; KUGLER and CAREY, 1970) and also values at 20°C (TILLOTSON and STAVELEY, 1958; and ANDEREGG, 1963) adjusted to 25°C using our ΔC_p values listed in Table 16.13. Values reported by CHRISTENSEN *et al.* (1969) seemed inconsistent with other results and were not included in the averages.

For association of $Na^+(aq)$ with $EDTA^{4-}(aq)$ there are several reported (CHRISTENSEN *et al.*, 1975; ANDEREGG, 1976; CHARLES, 1954; VASIL'EV and BELONOGOVA, 1976a) ΔH values from which the value from VASIL'EV and BELONOGOVA

(1976a) was chosen. From past experience with the enthalpy changes associated with these types of reactions, an uncertainty of about ± 2 kJ mol^{-1} is estimated for this value. For association of $K^+(aq)$ with $EDTA^{4-}(aq)$ a value $\Delta H \simeq 4$ kJ mol^{-1} was calculated [after correcting for the effect of temperature on the molarity (HEPLER, 1981) in the van't Hoff eq. 16.1] from equilibrium constants at several temperatures (DANIELE *et al.*, 1985) and also $\Delta H = 0 \pm 2$ kJ mol^{-1} from calorimetric measurements by VASIL'EV and BELONOGOVA (1976a); this latter value was chosen as the preferred value, which leads to a negligible relaxation contribution to the heat capacity (see Appendix A). All of these ΔH values used in our calculations are listed in Table 16.13.

16.5 Selections of ionic properties

For calculation of the temperature and pressure dependence of thermodynamic quantities (such as standard equilibrium constants), apparent molar heat capacities and volumes (identical to the corresponding partial molar properties at infinite dilution) are used. It is most convenient to tabulate these standard state quantities as the conventional ionic properties, based on $\bar{Y}^\circ(H^+, aq) \equiv 0$.

The selections of values for these conventional standard state quantities for $HEDTA^{3-}(aq)$ and for $H_2EDTA^{2-}(aq)$ are straightforward, based on the results in Table 16.11 in combination with properties listed in Table 16.10 for $Na^+(aq)$ and $(CH_3)_4N^+(aq)$. Results of these calculations are listed in the bottom half of Table 16.10.

Applications of Young's rule and the Pitzer model to extraction of standard state properties of $[(CH_3)_4N]_4EDTA$ from experimental results for solutions of $[(CH_3)_4N]_4$-EDTA + $(CH_3)_4NOH$ have led (Tables 16.3 and 16.8) to a small difference between the desired $\bar{V}^\circ$ values and to a substantial difference between the two $\bar{C}_p^\circ$ values that "should" be identical. In addition to this difference that comes from the two methods of data analysis, there are also different results from the two stock solutions that were used. Because there is no clear reason for selecting any one value of $\bar{C}_p^\circ$ or $\bar{V}^\circ$ as best, a weighted average of the various results was used, with appropriate consideration of the uncertainties. In this way $\bar{V}^\circ = 488 \pm 2$ cm^3mol^{-1} and $\bar{C}_p^\circ = 630$

± 20 J $K^{-1}mol^{-1}$ were selected as the best available values of these thermodynamic properties for $[(CH_3)_4N]_4EDTA(aq)$. These values then lead to the conventional ionic properties listed in Table 16.10 for $EDTA^{4-}(aq)$.

As can be seen in Tables 16.6 and 16.8, the two different methods of data analysis lead to somewhat different values for the properties of $Na_3[NaEDTA](aq)$ and $K_3[KEDTA](aq)$ at infinite dilution. These differences are due mostly to the differences in the properties of $[(CH_3)_4N]_4EDTA$ derived from the two methods of data analysis. Averages of values lead to $\bar{V}^\circ = 143.9 \pm 1$ cm^3mol^{-1} and $\bar{C}_p^\circ = 104 \pm 15$ J $K^{-1}mol^{-1}$ for $Na_3[NaEDTA](aq)$ and $\bar{V}^\circ = 178 \pm 2$ cm^3mol^{-1} and $\bar{C}_p^\circ = -51 \pm 25$ J $K^{-1}mol^{-1}$ for $K_3[KEDTA](aq)$. These values were used in calculating the conventional ionic standard state properties for $NaEDTA^{3-}(aq)$ and $KEDTA^{3-}(aq)$ that are listed in Table 16.10.

Many of the published thermodynamic results (equilibrium constants and enthalpies) for aqueous EDTA systems refer to solutions having constant ionic strength (mostly 0.1 molar), rather than to the infinite dilution condition that is appropriate to the selected ionic properties cited earlier in this section. The present results were therefore used to obtain partial molar heat capacities and volumes at this concentration by way of

$$\bar{Y} = {}^{\phi}Y + I\left(\frac{\partial {}^{\phi}Y}{\partial I}\right) \tag{16.30}$$

Results of these calculations are listed in Table 16.12, and related conventional properties of ionic species are listed in Table 16.10.

The only previous direct calorimetric investigation of heat capacities of EDTA solutions pertinent to this work was investigation of solutions of $H_2EDTA^{2-}(aq)$ (HOVEY and TREMAINE, 1985). VASIL'EV and BELONOGOVA (1975, 1976a,b,c, 1977) and VASIL'EV *et al.* (1983) have measured enthalpies of several reactions involving EDTA in moderately concentrated solutions over narrow (mostly 20°) ranges of temperature, with results that lead with eq. 16.2 to ΔC_p values for these same reactions. These ΔC_p values can be combined with results of previous direct heat capacity measurements (HOVEY and TREMAINE, 1985; Chapter 14) to provide estimates for the $\bar{C}_p^\circ$ of $EDTA^{4-}(aq)$. Results of these calculations are in poor agreement with the present direct value. The ΔH values derived by Vasil'ev and co-workers have

Table 16.12: Partial molar properties at $I = 0.10$ molal and 25°C from fits (for mixtures) based on Young's rule.

Solute	$\bar{V}_2^\dagger$ cm^3mol^{-1}	$\bar{C}_{p,2}^\dagger$ $(J\ K^{-1}mol^{-1})$
$[(CH_3)_4N]_4EDTA$	496	754
$Na_3[NaEDTA]$	148	197
$K_3[KEDTA]$	182	11
$[(CH_3)_4N]_3HEDTA$	422.8	677.1
Na_2H_2EDTA	157.0	221.7

been used and will be used for some thermodynamic calculations, but the derived ΔC_p values will not be used. VASIL'EV *et al.* have estimated that uncertainties in their derived ΔC_p values are about $\pm$ 50 J $K^{-1}mol^{-1}$. This estimate of uncertainties is optimistic because of inadequate allowance for the magnification of uncertainties associated with differentiation and also because of additional uncertainties in extrapolating their results to the standard states of present interest (infinite dilution or 0.1 molar or 0.1 molal). The present volumetric results for $H_2EDTA^{2-}(aq)$ are in excellent agreement with the results of HOVEY and TREMAINE (1985).

16.6 Thermodynamics of ionization reactions of EDTA

One of the principal purposes of this work has been to obtain partial molar heat capacities and volumes of species of EDTA, with a view toward using these results in thermodynamic calculations as described in the next section. Here (as in an earlier section) selections of various thermodynamic properties (K, ΔH, etc.) associated with the following ionization reactions of aqueous EDTA is of concern:

$$H_6EDTA^{2+}(aq) = H^+(aq) + H_5EDTA^+(aq) \tag{16.31}$$

$$H_5EDTA^+(aq) = H^+(aq) + H_4EDTA(aq) \tag{16.32}$$

$$H_4EDTA(aq) = H^+(aq) + H_3EDTA^-(aq) \tag{16.33}$$

$$H_3EDTA^-(aq) = H^+(aq) + H_2EDTA^{2-}(aq) \tag{16.34}$$

$$H_2EDTA^{2-}(aq) = H^+(aq) + HEDTA^{3-}(aq) \tag{16.35}$$

$$HEDTA^{3-}(aq) = H^+(aq) + EDTA^{4-}(aq) \tag{16.36}$$

$$H_6EDTA^{2+}(aq) = 6H^+(aq) + EDTA^{4-}(aq) \tag{16.37}$$

Equilibrium constants (K) and enthalpies (ΔH) for each of these reactions (16.31-16.37) have been selected as summarized earlier. The present experimental results lead to accurate values of ΔC_p and ΔV for reactions 16.35 and 16.36 and to less accurate values of ΔC_p and ΔV for reaction 16.34, as discussed earlier. These ΔC_p values are more reliable than those that can be obtained by way of application of $d\Delta H/dT$ to the enthalpy of reaction data of VASIL'EV *et al.* (1973, 1974, 1976,

1977a,b, 1978, 1979). The only experimental route that leads to ΔC_p for reaction 16.37 is by application of $d\Delta H/dT$ to the enthalpies of reaction measured in concentrated solution by VASIL'EV *et al.* (1977). Finally, ΔC_p values mentioned above have been used in constructing plots of ΔC_p against n (or alternatively against log K) for the ionization of $H_nEDTA^{n-4}(aq)$; these plots were used to *estimate* the "missing" ΔC_p values for reactions 16.31-16.33. Similar plots for ΔV values against log K for the ionization reactions 16.34-16.36 were used to *estimate* ΔV values for eqs. 16.31-16.33. These plots are shown in Figures 16.9 and 16.10. All of the selected (based on experimental and estimated results) thermodynamic quantities (K, ΔH, ΔC_p, and ΔV) for reactions 16.31-16.37 are collected in Table 16.13. Values for complexation of $Na^+(aq)$ and $K^+(aq)$ with $EDTA^{4-}(aq)$ are also listed in Table 16.13.

16.7 Extrapolations of equilibrium constants to higher temperatures

Equilibrium constants vary with temperature according to the van't Hoff equation 16.1 and the Kirchhoff equation 16.2 and vary with pressure according to

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta V^\circ}{RT} \tag{16.38}$$

Equations 16.1 and 16.2 can be combined with the specification that ΔC_p is (approximately) independent of temperature to obtain

$$\ln K_T^\dagger = \ln K_{298}^\dagger - \frac{\Delta H_{298}^\dagger}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right) + \frac{\Delta C_p^\dagger}{R}\left[\ln\left(\frac{T}{298.15}\right) + \frac{298.15}{T} - 1\right] \tag{16.39}$$

Here this equation is written in terms of the 0.1 molar reference state that is commonly used for EDTA studies. Experience has shown that equation 16.39 provides a much more accurate representation of the temperature dependence of equilibrium constants over wide ranges of temperature than does the simpler equation based on integration of eq. 16.1 with the pretence that ΔH is independent of temperature ($\Delta C_p = 0$).

In obtaining eq. 16.39, ΔC_p was specified to be (approximately) independent of temperature because there is no direct evidence about the possible temperature

Table 16.13: Thermodynamic parameters for the ionization of EDTA and complexation by $EDTA^{4-}(aq)$ at 0.1 molal or molar and 25°C.*

n	$M^+(aq)$	$\log K^\dagger$	$\Delta H^\dagger$ (kJ mol^{-1})	$\Delta S^\dagger$ ($JK^{-1}mol^{-1}$)	$\Delta \bar{C}_p^\dagger$ ($JK^{-1}mol^{-1}$)	$\Delta \bar{V}_2^\dagger$ (cm^3mol^{-1})
			$H_{4-n}EDTA^{n-}(aq) = H_{3-n}EDTA^{-(n+1)}(aq) + H^+(aq)$			
−2		(−1.20)	(4.5)	(−7.9)	(−152)	(−1.9)
−1		−1.51	−2.63	−37.7	(−152)	(−2.0)
0		−1.96	−1.32	−42.0	(−153)	(−2.2)
1		−2.68	−5.5	−69.8	−155[−183 ± 50]	−2.8
2		−6.19	18.2	−57.5	−155[−147 ± 50]	−4.4
3		−10.39	23.0	−122	−161[−98 ± 50]	−16.8
			$H_6EDTA^{2+}(aq) = 6H^+(aq) + EDTA^{4-}(aq)$			
		(−23.93)	36.3	−336	(−928)	(−30.1)
					(−853)†[−490 ± 60]†	(−29.7)†
			$M^+(aq) + EDTA^{4-}(aq) = MEDTA^{3-}(aq)$			
	Na^+	1.84	−8.45	6.9	198	14.1
	K^+	0.80	0.0	15.3	138	6.8
			$H_2O(l) = H^+(aq) + OH^-(aq)$			
		−13.78	56.62	−73.93	−197	−21.1

* Round bracketed values represent estimates of these values and square bracketed values represent $\partial \Delta H / \partial T$ results that were calculated previously (HOVEY and TREMAINE, 1985) from the results of VASIL'EV *et al.* (1973, 1974, 1976, 1977a,b, 1978).

† These values are estimates for the infinite dilution reference state.

dependence of this quantity for the reactions of present interest. Experience (BARBERO *et al.*, 1983; LINDSAY, 1980; MURRAY and COBBLE, 1980) has shown that ΔC_p values for "isocoulombic" reactions (symmetric with respect to number and charges of ions) are much more nearly independent of temperature than for electrically asymmetric reactions. It is therefore appropriate to focus on reactions 16.31, 16.32, and the following reactions that are related to 16.33-16.36, all of which are either isocoulombic or pseudo-isocoulombic:

$$EDTA^{4-}(aq) + H_2O(l) = HEDTA^{3-}(aq) + OH^-(aq) \qquad (16.40)$$

$$HEDTA^{3-}(aq) + H_2O(l) = H_2EDTA^{2-}(aq) + OH^-(aq) \qquad (16.41)$$

$$H_2EDTA^{2-}(aq) + H_2O(l) = H_3EDTA^-(aq) + OH^-(aq) \qquad (16.42)$$

$$H_3EDTA^-(aq) + H_2O(l) = H_4EDTA(aq) + OH^-(aq) \qquad (16.43)$$

Equilibrium constants, $\Delta H^\dagger$, and $\Delta C_p^\dagger$ values for reactions 16.40-16.43 are related to corresponding values for reactions 16.33-16.36 by $K^\dagger$, $\Delta H^\dagger$, and $\Delta C_p^\dagger$ for the ionization of water; $K^\dagger$ and $\Delta H^\dagger$ values were taken from earlier investigations (SWEETON *et al.*, 1974; OLOFFSON and HEPLER, 1975) and the values listed in Table 16.10 were used to calculate ΔC_p. All of these quantities quantities were used and application of eq. 16.39 to all of the ionization reactions of EDTA has resulted in the values listed in Table 16.14.

Integration of eq. 16.38 leads to

$$\ln K_p = \ln K_1 - (p-1)\frac{\Delta V^\dagger}{RT}(p-1) \qquad (16.44)$$

where ln $K_1^\dagger$ represents the value of the logarithm of $K^\dagger$ at 1 bar, and ln $K_p^\dagger$ the value at a pressure p. Although the effect of pressure on equilibrium constants is small at pressures up to the saturation pressure of water at 200°C, this effect has been included in the values listed in Table 16.14, calculated using saturation pressures of water from HAAR *et al.* (1984).

Results of similar calculations for the isocoulombic exchange reaction involving $NaEDTA^{3-}(aq)$ and $KEDTA^{3-}(aq)$ given by

$$K^+(aq) + NaEDTA^{3-}(aq) = KEDTA^{3-}(aq) + Na^+(aq) \qquad (16.45)$$

are listed along with the ionization constants in Table 16.14.

Table 16.14: Calculated equilibrium constants for some ionization reactions of H_4EDTA.*

	$\log K^\dagger$						
t	$H_{4-n}EDTA^{n-4}(aq) = H_{3-n}EDTA^{-(n+1)}(aq) + H^+(aq)$						Na^+/K^+
(°C)	$n=-2$	$n=-1$	$n=0$	$n=1$	$n=2$	$n=3$	exchange
0	−1.3	−1.50	−1.98	−2.64	−6.53	−10.80	1.19
20	−1.2	−1.50	−1.98	−2.68	−6.26	−10.48	1.07
25	−1.2	−1.51	−1.96	−2.68	−6.19	−10.39	1.04
37	−1.2	−1.53	−2.00	−2.75	−6.10	−10.27	0.99
50	−1.2	−1.57	−2.01	−2.79	−5.97	−10.11	0.94
75	−1.2	−1.67	−2.08	−2.91	−5.82	−9.90	0.86
100	−1.2	−1.79	−2.17	−3.04	−5.71	−9.75	0.82
125	−1.3	−1.93	−2.27	−3.18	−5.65	−9.65	0.79
150	−1.4	−2.08	−2.38	−3.33	−5.61	−9.58	0.77
175	−1.5	−2.24	−2.51	−3.48	−5.60	−9.54	0.77
200	−1.6	−2.41	−2.66	−3.66	−5.63	−9.55	0.78
250	−1.9	−2.76	−2.97	−4.02	−5.74	−9.62	0.81

* The uncertainties in these values depend on the uncertainties in the values of $\log K^\dagger$ at 25°C and in the extrapolation. Experience has shown that errors in $\log K$ due to the extrapolations increase to about ± 0.5 at 250°C.

16.8 References

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Appendix A

Relaxation contributions to heat capacities of mixed electrolyte solutions

There have been several accounts (WOOLLEY and HEPLER, 1977; LARSON *et al.*, 1982, MAINS *et al.*, 1984; JOLICOEUR *et al.*, 1979; Chapter 5) of the contributions of chemical relaxation to heat capacities of aqueous solutions of electrolytes, but none has dealt with the kinds of mixed electrolyte effects encountered here.

The total enthalpy of a system containing k components can be expressed (MAINS *et al.*, 1984) by

$$H = \sum_k n_k H_k \qquad (A.1)$$

in which n_k and H_k represent the number of moles and the partial molar enthalpy of the k'th component. Differentiation with respect to temperature leads to

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \sum_k n_k \left(\frac{\partial H_k}{\partial T}\right)_p + \sum_k H_k \left(\frac{\partial n_k}{\partial T}\right)_p \qquad (A.2)$$

In this equation the first summation term represents the "compositional" or "species" contribution to the heat capacity and the second summation term represents the contribution to the heat capacity due to the change in distribution (chemical relaxation) of species induced by the change of temperature that is necessary for heat capacity measurements. The last term (relaxation contribution to the heat capacity) must be subtracted from the measured heat capacity to obtain the compositional contribution of the chemical species of interest.

Evaluation of the relaxation contribution for mixed aqueous electrolyte solutions of present interest can begin along the lines of an earlier investigation (WOOLLEY and HEPLER, 1977) by expressing the heat capacity C_p of a solution (containing 1 kg of water) as a sum of compositional or species and relaxation contributions denoted

by superscripts *sp* and *rel* as in

$$C_p(\text{sol}) = \left(\frac{\partial H}{\partial T}\right)_p^{sp} + \left(\frac{\partial H}{\partial T}\right)_p^{rel} \qquad (A.3)$$

Combination of this equation with a defining equation (see equation 16.3) gives

$${}^{\phi}C_{p,\Sigma}^{exp} = \frac{\left(\frac{\partial H}{\partial T}\right)_p^{sp} - C_p(\text{H}_2\text{O})}{m_2 + m_3} + \frac{\left(\frac{\partial H}{\partial T}\right)_p^{rel}}{m_2 + m_3} \qquad (A.4)$$

A start on the evaluation of the relaxation term in eq. A.4 is provided (WOOLLEY and HEPLER, 1977) by

$$\left(\frac{\partial H}{\partial T}\right)_p^{rel} = \left(\frac{\partial H}{\partial(\alpha m_2)}\right)_p \left(\frac{\partial(\alpha m_2)}{\partial T}\right)_{p,m_2} = m_2 \Delta H \left(\frac{\partial \alpha}{\partial T}\right)_{p,m_2} \qquad (A.5)$$

in which α is the fractional extent of the reaction, m_2 is the stoichiometric molality of the reacting electrolyte, and ΔH is the molar enthalpy of the reaction. Now the expression

$${}^{\phi}C_{p,\Sigma}^{rel} = \frac{m_2}{m_2 + m_3} \Delta H \left(\frac{\partial \alpha}{\partial T}\right)_{p,m_2} \qquad (A.6)$$

represents the contribution of chemical relaxation to the apparent molar heat capacities that come directly from the calorimetric measurements on solutions discussed in the Chapter. Evaluation of $(\partial\alpha/\partial T)_{p,m}$ is done in terms of the equilibrium constant K, the temperature dependence of K as in eq. 16.1, activity coefficients, and the temperature dependence of the activity coefficients. Because of limitations imposed by the available data, the distinction between ΔH and $\Delta H°$ (related to the temperature dependence of activity coefficients) has been ignored and also K values were used that refer to specified concentrations and were expressed in terms of concentrations of various species.

1.1 Solutions of Na_3[NaEDTA] and K_3[KEDTA]

The equilibrium reaction to be considered in connection with these solutions was represented by eq. 16.10 in the main text. Mathematical manipulation of K for reaction 16.10 expressed in terms of α in combination with eq. 16.1 leads to

$$\left(\frac{\partial \alpha}{\partial T}\right)_{p,m_2} = \frac{K \Delta H (1 - \alpha)}{RT^2(3m_2 + 2\alpha m_2 + m_3 + K)} \qquad (A.7)$$

K values (given as a function of ionic strength) were taken from DANIELE *et al.* (1985) as listed in Table 16.4, and ΔH = -8.5 kJ mol^{-1} (Chapter 16) to evaluate the relaxation contributions to the heat capacities of solutions of Na_3[NaEDTA] + NaOH as listed in Table A.1. Because $\Delta H \simeq 0$ for the corresponding reaction involving K^+(aq), the relaxation contribution for these solutions is nearly zero.

1.2 Solutions containing $HEDTA^{3-}$(aq) and H_2EDTA^{2-}(aq)

The relaxation components of the experimental apparent molar heat capacities of solutions containing $HEDTA^{3-}$(aq) and H_2EDTA^{2-}(aq) are given by the usual (Chapter 5) expressions for coupled reactions (α and β defined in terms of eqs. 16.24, 16.25, and 16.27,16.28):

$$^{\phi}C^{rel}_{p,\alpha} = \Delta H_\alpha \left(\frac{\partial \alpha}{\partial T}\right)_{p,m} \qquad (A.8)$$

$$^{\phi}C^{rel}_{p,\beta} = \Delta H_\beta \left(\frac{\partial \beta}{\partial T}\right)_{p,m} \qquad (A.9)$$

Mathematical manipulations with equilibrium constants for two coupled equilibria in combination with eq. 16.1 lead to complicated expressions for $(\partial\alpha/\partial T)_{p,m}$ and $(\partial\beta/\partial T)_{p,m}$ that are similar to expressions from other systems of coupled equilibria, some of which are discussed in more detail elsewhere (Chapter 5; MAINS *et al.*, 1984). Values of ΔH were selected and used in eqs. A.8 and A.9 and it was found that the relaxation components of the heat capacities are negligibly small for solutions in which $HEDTA^{3-}$(aq) is the principal species of interest, and also non-negligible relaxation contributions to the heat capacities of solutions of H_2EDTA^{2-}(aq) as listed in Table A.2.

Table A.1: Relaxation contributions to heat capacities of solutions of $Na_3NaEDTA$ + NaOH.

m_2 (mol kg^{-1})	$10^2\alpha$	$-10^4\left(\frac{\partial\alpha}{\partial T}\right)_m$ (K^{-1})	${}^{\phi}C_p^{rel}$ (J K^{-1}mol^{-1})	${}^{\phi}C_{p,\Sigma}^{rel}$ (J K^{-1}mol^{-1})	${}^{\phi}C_{p,\Sigma}^{exp}$ (J K^{-1}mol^{-1})	${}^{\phi}C_{p,\Sigma}$ (J K^{-1}mol^{-1})
0.2057	1.88	1.99	1.59	0.89	162.3	161.4
0.1744	2.10	2.22	1.78	0.94	139.8	138.4
0.1552	2.32	2.44	1.95	0.98	123.5	122.5
0.1321	2.67	2.80	2.24	1.05	103.2	102.2
0.1168	2.99	3.12	2.49	1.10	88.67	87.58
0.09857	3.48	3.61	2.89	1.16	69.81	68.65
0.07562	4.35	4.46	3.57	1.24	42.28	41.04
0.05594	5.40	5.48	4.39	1.25	17.13	15.88
0.03969	6.58	6.59	5.27	1.18	−5.82	−6.998
0.02053	8.41	8.27	6.62	0.87	−39.89	−40.76

Table A.2: Relaxation contributions to heat capacities of solutions of Na_2H_2EDTA.

m_2 (mol kg^{-1})	$10^2\alpha$	$10^2\beta$	$10^4\left(\frac{\partial\alpha}{\partial T}\right)_m$ (K^{-1})	$10^4\left(\frac{\partial\beta}{\partial T}\right)_m$ (K^{-1})	${}^{\phi}C_{p,\alpha}^{rel}$ (J K^{-1}mol^{-1})	${}^{\phi}C_{p,\beta}^{rel}$ (J K^{-1}mol^{-1})	${}^{\phi}C_{p}^{exp}$ (J K^{-1}mol^{-1})	${}^{\phi}C_{p}^{exp} - {}^{\phi}C_{p,tot}^{rel}$ (J K^{-1}mol^{-1})
0.2588	1.76	1.74	2.84	2.83	5.54	1.53	285.1	278.0
0.1631	1.78	1.75	2.88	2.85	5.60	1.55	261.0	253.9
0.1251	1.78	1.75	2.88	2.85	5.61	1.54	248.0	240.9
0.1015	1.78	1.74	2.88	2.84	5.61	1.54	240.4	233.2
0.06069	1.77	1.71	2.86	2.80	5.57	1.52	221.9	214.8
0.03530	1.75	1.65	2.82	2.72	5.49	1.47	208.0	201.0
0.02597	1.74	1.61	2.79	2.67	5.44	1.45	204.1	197.3

Chapter 17

Thermodynamics of aqueous metal-ion complexation by ethylenediaminetetraacetic acid (EDTA): Recommended thermodynamic properties for selected reactions at 25°C

17.1 Introduction

The thermodynamic properties associated with aqueous metal-ion complexation by EDTA have been the focus of several specific reviews [see for example ANDEREGG (1977)] and also as parts of large compilations for many metal-ion complexation reactions (SILLÉN and MARTELL, 1964, 1971; MARTELL and SMITH, 1976; HÖGFELDT, 1982; CHRISTENSEN *et al.*, 1975). Several studies (HOVEY and TREMAINE, 1985; Chapters 14-16) have led to the evaluation of standard state partial molar heat capacities and volumes of several aqueous metal-ion EDTA complexes. As mentioned in all of these works, the presently available thermodynamic data (equilibrium constants or Gibbs free energies, enthalpies, and entropies] have been determined under a wide variety of conditions. The majority of data have been obtained at 25°C and an ionic strength of 0.1 molar or molal, although several other temperatures and ionic strengths have also been investigated.

Useful equations that show the relationship of standard state partial molar volumes and heat capacities to equilibrium constants and enthalpies of reaction are the following:

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2} \tag{17.1}$$

$$\left(\frac{\partial \Delta H^\circ}{\partial T}\right)_p = \Delta C_p^\circ \tag{17.2}$$

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = \frac{-\Delta V^\circ}{RT} \tag{17.3}$$

A principal aim of this review is to select the "best" equilibrium constants, enthalpies, and other thermodynamic properties for reactions of type 17.4 for several metal ions. The starting point for most of the work is provided by ANDEREGG (1977). The reaction of EDTA with aqueous metal ions is pH dependent because of the various protonation states of the pure acid H_4EDTA. It has been customary to work under conditions such that H_4EDTA is completely ionized. The complexation reaction of importance under these conditions is written as

$$M^{z+}(aq) + EDTA^{4-}(aq) = MEDTA^{z-4}(aq) \qquad (17.4)$$

The procedure for selecting "best" thermodynamic values for metal-ion EDTA complexation reactions will be to use the relationship between partial molar heat capacities and enthalpies to convert all measured enthalpies to a single reference temperature, 298.15 K and to use these values in further calculations as described below.

17.2 Evaluation of "best" properties

The general approach here will be to select "best" available enthalpies for reactions of type 17.4. Preference will be given to those values obtained calorimetrically. For some metal ions we also consider enthalpies that can be calculated by way of eq. 17.1. Enthalpies corresponding to the reaction given by eq. 17.4 were taken from those studies listed by CHRISTENSEN *et al.* (1975) and also some more recent investigations. The standard state heat capacities and volumes of the aqueous metal-ion EDTA complexes can be converted into the corresponding partial molar properties at 0.1 molal by standard thermodynamic relations. These properties can then be used to convert enthalpies determined at 0.1 molal and some other temperature to our selected reference temperature 298.15 K.

17.2.1 Ionization reactions of H_4EDTA

The thermodynamic properties for the ionization of EDTA are required in several calculations that follow. The ionization reactions of H_4EDTA can be represented generally by

$$H_{4-n}EDTA^{n-}(aq) = H_{3-n}EDTA^{-(n+1)}(aq) + H^{+}(aq) \qquad (17.5)$$

where n can range from –2 to +3.

Selections of equilibrium constants and enthalpies of reaction for various steps (Chapter 16; HOVEY and TREMAINE, 1985) have been previously outlined. The selections in Chapter 16 for an ionic strength of 0.1 molar represent values accurate to within expected uncertainties of other "best" values such as those selected by ANDEREGG (1977). These values were derived with careful consideration of the weak complexes formed by EDTA with sodium and potassium ions at high concentrations of hydroxide ion. The changes in the Gibbs free energies for the ionization reactions represented by $n = 0$ to 3 were taken solely from the work of DANIELE *et al.* (1985) pertaining to an ionic strength of 0.1 molar in solutions of non-complexing tetraalkylammonium halides. The selected value for $n = 0$ is in excellent agreement with the value selected by ANDEREGG (1977) and that for $n = 3$ is within stated uncertainties (DANIELE *et al.*, 1985). All of the selected values from Anderegg pertain to an ionic strength of 0.1 molar in aqueous KNO_3 solutions. Anderegg's listing of equilibrium constants for an ionic strength medium of tetramethylammonium chloride (WATTERS and SCHUPP, 1968) are in excellent agreement with the present selections, indicating that these are the preferred values. The equilibrium constant data for the two protonation reactions of $H_4EDTA(aq)$ are much less certain than the other values. The value listed by ANDEREGG (1977) was chosen for the first protonation step of H_4EDTA and also the recommendations of ANDEREGG (1977) and VASIL'EV *et al.* (1979) were considered in estimating $\log K^{\dagger}$ = -1.2 ± 0.6 for protonation of $H_5EDTA^{+}(aq)$, by considering the trends in all of the other equilibrium constants of $H_4EDTA(aq)$ at 0.1 molar as described in Chapter 16. The superscript † refers to those properties pertaining to the reference state of 0.1 molal or molar.[1]

The partial molar volumes and heat capacities at 0.1 molal for all of the ionized species of EDTA were derived from measurements on aqueous solutions containing the species $H_2EDTA^{2-}(aq)$, $HEDTA^{3-}(aq)$ and $EDTA^{4-}(aq)$ that are described in

[1]The heat capacity results that pertain to an ionic strength of 0.1 molal are assumed to be equal to those at 0.1 molar. This approximation will have no affect on enthalpies of reaction converted to the present reference temperature. The difference between molality and molarity becomes important when enthalpies of reaction are derived from equilibrium constants obtained as a function of temperature. These considerations are discussed elswhere in this thesis and more completely by HEPLER (1981).

Chapter 16. Results of these measurements can be used to derive the appropriate changes in heat capacities for the reactions represented by eq. 17.5. These $\Delta C_p^\dagger$ values can then be used to convert enthalpies obtained at temperatures other than 25°C to 25°C. All enthalpies obtained by a calorimetric procedure are presented later in Table 17.1. The recommended value cited for each ionization reaction is based on a weighted average of the available "adjusted" data. Measurements done under conditions where negligible complexation is thought to occur between EDTA and the supporting electrolyte are weighted more heavily than others. The values reported by CHRISTENSEN *et al.* (1969) seemed inconsistent with other results and were not included in any of the averages. As discussed previously, expressions reported by the original authors for the ionic strength dependences of the enthalpy changes associated with the ionization reactions (based on Debye-Hückel theory expressions) were used in some cases (particularly in the studies by VASIL'EV and co-workers) to extrapolate more highly concentrated results to the 0.1 molar reference state.

17.2.2 Metal-ion complexation reactions

For many metal ions that are not especially difficult to handle such as most of the main row transition metals, the available stability constants are generally in good agreement. The best compilations and selections are those of MARTELL and SMITH (1974) and ANDEREGG (1977), although the latter recommends values mostly pertaining to 20°C (rather than 25°C as done here) and 0.1 molar KNO_3. The values selected by MARTELL and SMITH (1974) were accepted here for most of the metal-ion complexation reactions. These selections are mostly in very good agreement with the selections of Anderegg considering the difference in temperature. Equilibrium constants for the complexation reactions with the alkali metal ions were not taken from MARTELL and SMITH (1974) as discussed following the description of enthalpy selections.

Calorimetrically obtained enthalpies for selected metal-ion reactions are reported in Table 17.1 Several studies show regular deviations from our "recommended" values. All of the results from Vasil'ev and co-workers are more negative than our selections while those of Care and Staveley are more positive (after being converted to 25°C with the heat capacity functions presented in Table 17.2). The results of

Table 17.1: Critically evaluated constants for EDTA ionization and complexation at an ionic strength of 0.1 molar and 25°C.*

$\Delta H^\dagger$ kJ mol^{-1}	Reference	Original conditions
	$H_6EDTA^{2+}(aq) = H_4EDTA^{+}(aq) + 2H^{+}(aq)$	
31.4±1	VASIL'EV *et al.* (1977b)	I=0, HNO_3, $HClO_4$, HCl, 25°
	$H_6EDTA^{2+}(aq) = H_4EDTA^{+}(aq) + 2H^{+}(aq)$	
1.9±1	VASIL'EV *et al.* (1979)	I=0, HNO_3, $HClO_4$, 25°
	$H_5EDTA^{+}(aq) = H_4EDTA^{-}(aq) + H^{+}(aq)$	
-2.8±1	TILLOTSON and STAVELEY (1958)	0.1M KCl, 20°C
	$H_4EDTA(aq) = H_3EDTA^{-}(aq) + H^{+}(aq)$	
-1.4±1.0	*Recommended*	
-1.52	TILLOTSON and STAVELEY (1958)	0.1 m KCl, 20°C
-1.32	VASIL'EV *et al.* (1973,1976)	0.1 m KNO_3, 25°C
	$H_3EDTA^{-}(aq) = H_2EDTA^{2-}(aq) + H^{+}(aq)$	
-5.9±1	*Recommended*	
-5.42	VASIL'EV *et al.* (1973,1976)	0.1M KNO_3, 25°C
-6.64	TILLOTSON and STAVELEY (1958)	0.1M KCl, 20°C
	$H_2EDTA^{2-}(aq) = HEDTA^{3-}(aq) + H^{+}(aq)$	
18.2±1	*Recommended*	
19.5	VASIL'EV *et al.* (1974,1978)	0.1M KNO_3, 25°C
17.6	TILLOTSON and STAVELEY (1958)	0.1M KCl, 20°C
17.4	ANDEREGG (1963)	0.1M KNO_3, 20°C
18.2	KUGLER and CAREY (1970)	0.1M KNO_3, 25°C
15.1	CHRISTENSEN *et al.* (1969)	< .01M EDTA, 25°C
	$HEDTA^{3-}(aq) = EDTA^{4-}(aq) + H^{+}(aq)$	
23.0±0.5	*Recommended*	
22.80	VASIL'EV *et al.* (1974,1976)	0.1M KNO_3, 25°C

$\Delta H^{\dagger}$ kJ mol^{-1}	Reference	Original conditions
23.0	TILLOTSON and STAVELEY (1958)	0.1M KCl, 20°C
22.9	ANDEREGG (1963)	0.1M KNO_3, 20°C
23.4	KUGLER and CAREY (1970)	0.1M KNO_3, 25°C
18.2	CHRISTENSEN *et al.* (1969)	< .01M EDTA, 25°C
	$Na^+(aq) + EDTA^{4-}(aq) = NaEDTA^{3-}(aq)$	
-8.5±2	*Recommended*	
-8.66	VASIL'EV and	0.1M KNO_3, 25°C
-8.45	BELONOGOVA (1976a)	0.1M $(CH_3)_4NCl$, 25°C
-6	CHARLES (1954)	< 0.1M Na_4EDTA, 25°C
-9.8	ANDEREGG (1976)	1M $(CH_3)_4NCl$, 20°C
-4.4		0.1M NaCl, 20°C
	$K^+(aq) + EDTA^{4-}(aq) = KEDTA^{3-}(aq)$	
0±3	*Recommended*	
4‡	DANIELE *et al.* (1985)	0.1M KNO_3, 25°C
0	VASIL'EV and BELONOGOVA (1976a)	0.1M $(CH_3)_4NNO_3$, 25°C
	$Mg^{2+}(aq) + EDTA^{4-}(aq) = MgEDTA^{2-}(aq)$	
15.1±1	*Recommended*	
13.9	VASIL'EV and BELONOGOVA (1975)	0.1M KNO_3, 25°C
14	CHARLES (1954)	< 0.1M Na_4EDTA, 25°C
14.9	CARE and STAVELEY (1956)	0.1M KNO_3, 25°C
23	JORDAN and ALLEMAN (1957)	0.01M Na_4EDTA, 25°C
16.4	ANDEREGG (1963)	0.1M KNO_3, 20°C
	$Ca^{2+}(aq) + EDTA^{4-}(aq) = CaEDTA^{2-}(aq)$	
-25.8±1.3	*Recommended*	
-28.08	VASIL'EV and BELONOGOVA (1976b)	0.1M KNO_3, 25°C
-27	CHARLES (1954)	< 0.1M Na_4EDTA, 25°C
-26.2	CARE and STAVELEY (1956)	0.1M KNO_3, 25°C
-24	JORDAN and ALLEMAN (1957)	0.01M Na_4EDTA, 25°C
-25.7	ANDEREGG (1963)	0.1M KNO_3, 20°C
-24.0	YATSIMIRSKII and KARACHEVA (1959)	0.06M EDTA, 25°C

$\Delta H^{\dagger}$ kJ mol^{-1}	Reference	Original conditions
	$Sr^{2+}(aq) + EDTA^{4-}(aq) = SrEDTA^{2-}(aq)$	
-17.2±2.1	*Recommended*	
-19.8	VASIL'EV and BELONOGOVA (1987)	0.1M $NaClO_4$, 25°C
-18	CHARLES (1954)	< 0.1M Na_4EDTA, 25°C
-15.6	CARE and STAVELEY (1956)	0.1M KNO_3, 25°C
-15.5	ANDEREGG (1963)	0.1M KNO_3, 20°C
	$Ba^{2+}(aq) + EDTA^{4-}(aq) = BaEDTA^{2-}(aq)$	
-20.4±1.3	*Recommended*	
-28.08	VASIL'EV *et al.* (1983)	0.1M $NaClO_4$, 25°C
-21	CHARLES (1954)	< 0.1M Na_4EDTA, 25°C
-18.3	CARE and STAVELEY (1956)	0.1M KNO_3, 25°C
-18.7	ANDEREGG (1963)	0.1M KNO_3, 20°C
-22	WRIGHT *et al.* (1965)	0.1M KNO_3, 25°C
	$Mn^{2+}(aq) + EDTA^{4-}(aq) = MnEDTA^{2-}(aq)$	
-19.0±2.6	*Recommended*	
-22	CHARLES (1954)	< 0.1M Na_4EDTA, 25°C
-17.5	ANDEREGG (1963)	0.1M KNO_3, 20°C
	$Co^{2+}(aq) + EDTA^{4-}(aq) = CoEDTA^{2-}(aq)$	
-17.5±1.3	*Recommended*	
-19.0	VASIL'EV and BELONOGOVA (1976c)	0.1M KNO_3, 25°C
-17	CHARLES (1954)	< 0.1M Na_4EDTA, 25°C
-18	JORDAN and ALLEMAN (1957)	0.01M Na_4EDTA, 25°C
-15.9	ANDEREGG (1963)	0.1M KNO_3, 20°C
	$Ni^{2+}(aq) + EDTA^{4-}(aq) = NiEDTA^{2-}(aq)$	
-32.0±2.3	*Recommended*	
-31.1	VASILEV and BELONOGOVA (1976c)	0.1M KNO_3, 25°C
-32	CHARLES (1954)	< 0.1M Na_4EDTA, 25°C
-33.3	CARE and STAVELEY (1956)	0.1M KNO_3, 25°C
-31	JORDAN and ALLEMAN (1957)	0.01M Na_4EDTA, 25°C

$\Delta H^{\dagger}$ kJ mol^{-1}	Reference	Original conditions
-29.9	ANDEREGG (1963)	0.1M KNO_3, 20°C
-36	WRIGHT *et al.* (1965)	0.1M KNO_3, 25°C
	$Cu^{2+}(aq) + EDTA^{4-}(aq) = CuEDTA^{2-}(aq)$	
-34.9±1.7	*Recommended*	
-36.6	VASILEV and BELONOGOVA (1977)	0.1M KNO_3, 25°C
-34	CHARLES (1954)	< 0.1M Na_4EDTA, 25°C
-34.7	CARE and STAVELEY (1956)	0.1M KNO_3, 25°C
-34	JORDAN and ALLEMAN (1957)	0.01M Na_4EDTA, 25°C
-32.5	ANDEREGG (1963)	0.1M KNO_3, 20°C
-37	WRIGHT *et al.* (1965)	0.1M KNO_3, 25°C
	$Zn^{2+}(aq) + EDTA^{4-}(aq) = ZnEDTA^{2-}(aq)$	
-20.5±1.9	*Recommended*	
-19	CHARLES (1954)	< 0.1M Na_4EDTA, 25°C
-21.8	CARE and STAVELEY (1956)	0.1M KNO_3, 25°C
-19	JORDAN and ALLEMAN (1957)	0.01M Na_4EDTA, 25°C
-18.7	ANDEREGG (1963)	0.1M KNO_3, 20°C
-23	WRIGHT *et al.* (1965)	0.1M KNO_3, 25°C
	$Cd^{2+}(aq) + EDTA^{4-}(aq) = CdEDTA^{2-}(aq)$	
-39.4±2.6	*Recommended*	
-38	CHARLES (1954)	< 0.1M Na_4EDTA, 25°C
-40.7	CARE and STAVELEY (1956)	0.1M KNO_3, 25°C
-39	JORDAN and ALLEMAN (1957)	0.01M Na_4EDTA, 25°C
-36.4	ANDEREGG (1963)	0.1M KNO_3, 20°C
-42	WRIGHT *et al.* (1965)	0.1M KNO_3, 25°C
	$Hg^{2+}(aq) + EDTA^{4-}(aq) = HgEDTA^{2-}(aq)$	
-78.3±1.8	*Recommended*	
-78.3	ANDEREGG (1963)	0.1M KNO_3, 20°C
-80	WRIGHT *et al.* (1965)	0.1M KNO_3, 25°C

$\Delta H^{\dagger}$ kJ mol^{-1}	Reference	Original conditions
	$Pb^{2+}(aq) + EDTA^{4-}(aq) = PbEDTA^{2-}(aq)$	
-53.9±1	*Recommended*	
-57.2	CARE and STAVELEY (1956)	0.1M KNO_3, 25°C
-54	JORDAN and ALLEMAN (1957)	0.01M Na_4EDTA, 25°C
-53.5	ANDEREGG (1963)	0.1M KNO_3, 20°C
-54.8	WRIGHT *et al.* (1965)	0.1M KNO_3, 25°C
	$Al^{3+}(aq) + EDTA^{4-}(aq) = AlEDTA^{-}(aq)$	
54±3	*Recommended*	
55.5	STAVELEY and RANDALL (1958)	0.1M KNO_3, 20°C
51	MOELLER and CHU (1966)	0.2M KNO_3, 20°C
51	YATSIMIRSKII and KARACHEVA (1958)	0.22M EDTA, 25°C
	$Fe^{3+}(aq) + EDTA^{4-}(aq) = FeEDTA^{-}(aq)$	
-11.5±3	Recommended	
-41.6‡	BORGGAARD (1972)	I=0.2M 10-40°C
-11.5	DOI (1978)	0.1M $HClO_4$, $NaClO_4$, 25°C

* Original experimental conditions for some studies are exactly as shown. For the works of VASIL'EV *et al.* the original measurements were made using a variety of different supporting electrolytes and also over a range of ionic strengths. Because we believe the results with KNO_3 are most reliable, these were calculated at 0.1 molar from reported ionic strength expressions.

‡ These values are based on differentiation of equilibrium constants obtained as a function of temperature.

JORDAN and ALLEMAN (1957) were not included in any averages because of our belief that all of the other values are more reliable. Results reported by CHARLES (1954) and WRIGHT *et al.* (1965) were consistently weighted lower than the other results because of these same expectations. All "recommended" values in the Table come from weighted averages of the listed values in accord with the the conditions of the measurement (original temperature, ionic strength, etc.) and our belief of accuracies among different workers (mostly discussed above).

The recommended values listed in Table 17.1 are not significantly different than the selections in Chapters 14 and 15 or those reported by HOVEY and TREMAINE (1985). However, all of these previous values were based on averages of enthalpies adjusted to 25°C using heat capacity values for the ionization of H_4EDTA obtained by temperature dependent enthalpy measurements by VASIL'EV *et al.* (1973,1974,1976, 1977a,1977b,1978,1979). These new selections are based on the direct measurement of the heat capacity change associated with the ionization of $H_2EDTA^{2-}(aq)$ as reported in Chapter 16. For two of the reactions presented in Table 17.1, enthalpies calculated by way of temperature dependent equilibrium constants are included because of the lack of calorimetric data for these reactions.

17.3 Recommended thermodynamic properties

The critical selections of the enthalpy values associated with all of the reactions listed in Table 17.1 can be used along with equilibrium constants from MARTELL and SMITH (1974) to generate recommended values for the entropy change associated with the ionization reactions of EDTA and also several metal-ion complexation reactions. These values along with the volume and heat capacity changes provide most desired thermodynamic properties.

As mentioned earlier, all equilibrium constants were taken from Smith and Martell except the following values. Equilibrium constants for the weak alkali metal complexes were not taken from MARTELL and SMITH (1974) because of the availability of more modern data. Several investigations (DANIELE *et al.*, 1985; ANDEREGG, 1977; SCHWARZENBACH and ACKERMANN, 1947; WATTERS and SCHUPP, 1968; PALATY, 1963; BOTTS *et al.*, 1965; CARR and SWARTZFAGER, 1973; ANDEREGG,

1967) have led to values of the equilibrium constant for association of $Na^+(aq)$ with $EDTA^{4-}(aq)$; here the results of DANIELE *et al.* (1985) were selected. The chosen equilibrium constants for association of $K^+(aq)$ with $EDTA^{4-}(aq)$ reported by DANIELE *et al.* (1985) are in good agreement with results from others (WATTERS and SCHUPP, 1968; BOTTS *et al.*, 1965; CARR and SWARTZFAGER, 1973) and are used in further calculations.

Now that equilibrium constants and enthalpies are available for each of the reactions of present interest, the changes in the partial molar entropies at 0.1 molar and 25°C can be calculated by the fundamental expression

$$\Delta S^\dagger = \frac{\Delta H^\dagger + \ln(10) RT \log K^\dagger}{T} \tag{17.6}$$

All of the selected values and corresponding calculations (entropy changes) from these selections are presented in Table 17.2.

17.4 Trends in thermodynamic properties

Although the purpose of the present work is not to identify the structural effects of the EDTA-complexes or the solute-solvent interactions responsible for the observed thermodynamic properties,[2] it is of use to note regular trends in the selected data. These trends are especially important for changes in partial molar heat capacities since estimated values (if reliable) could be used to refine enthalpy values which lead to refined entropy changes.

CHARLES (1954) noted that conventional standard state entropies of ions plotted against his estimates of the changes in the standard state entropies for metal-ion complexation were approximately linear. Changes in entropy at 0.1 molar for the metal-ion complexation reactions are plotted versus "absolute" entropies of the metal ions in Figure 17.1 These absolute properties were calculated using $\bar{S}_{abs}(H^+, aq) = -22$ J $K^{-1}mol^{-1}$ from CONWAY (1978). Absolute properties are related to conventional ionic properties $\bar{S}_{abs}(H^+, aq) = 0$ by

$$\bar{S}_{abs} = \bar{S}^\circ + z\bar{S}_{abs}(H^+, aq) \tag{17.7}$$

[2] An extensive account of these effects and several more theoretical explanations for the observed thermodynamic properties is in preparation by the author.

Table 17.2: Selected thermodynamic parameters for the ionization of EDTA and for selected metal-ion complexation reactions with $EDTA^{4-}(aq)$ at 0.1 molal or molar and 25°C.*

n / M^{z+}	$\log K^{\dagger}$	$\Delta H^{\dagger}$ (kJ mol^{-1})	$\Delta S^{\dagger}$ ($JK^{-1}mol^{-1}$)	$\Delta \bar{C}_p^{\dagger}$ ($JK^{-1}mol^{-1}$)	$\Delta \bar{V}_2^{\dagger}$ (cm^3mol^{-1})
		$H_{4-n}EDTA^{n-}(aq) = H_{3-n}EDTA^{-(n+1)}(aq) + H^+(aq)$			
-2	(-1.20)	(4.7)	(-7.2)	(-152)	(-1.9)
-1	-1.51	-2.8	-38.3	(-152)	(-2.0)
0	-1.96	-1.4	-42.2	(-153)	(-2.2)
1	-2.68	-5.9	-71.1	-155	-2.8
2	-6.19	18.2	-57.5	-155	-4.4
3	-10.39	23.0	-122	-161	-16.8
		$M^{z+}(aq) + EDTA^{4-}(aq) = MEDTA^{z-4}(aq)$			
Na^+	1.84	-8.5	6.9	198	14.1
K^+	0.80	0.0	15.3	138	6.8
Mg^{2+}	8.83	15.1	169	351	52.4
Ca^{2+}	10.61	-25.8	117	349	39.1
Sr^{2+}	8.68	-17.2	109	323	43.1
Ba^{2+}	7.80	-20.4	81	387	41.2
Mn^{2+}	13.81	-19.0	201	317	43.5
Co^{2+}	16.26	-17.5	253	334	57.5
Ni^{2+}	18.52	-32.0	247	330	57.8
Cu^{2+}	18.70	-34.9	251	311	55.2
Zn^{2+}	16.44	-20.5	246	327	57.4
Cd^{2+}	16.36	-39.4	181	299	43.3
Hg^{2+}	21.5	-78.3	149	368	46.3
Pb^{2+}	17.88	-53.9	162	340	59.0
Al^{3+}	16.5	54	497	573	74.4
Fe^{3+}	25.0	-11.5	440	544	67.4

* Round bracketed values represent estimates

Conventional ionic entropies for all of the metal cations were taken from the NBS tables (WAGMAN *et al.*, 1982), $\Delta S^{\dagger}$ values were those listed in Table 17.2 for these ions and values for several other ions were taken directly from MARTELL and SMITH (1974).

As can be seen in the figure, there is a reasonably linear relationship between these absolute properties and $\Delta S^{\dagger}$. As indicated on the graph the deviations from linearity all fall within the entropy of one mole of bulk water (69.9 J $K^{-1}mol^{-1}$). The observed differences are attributed to differences in the state of complexation (of the $MEDTA^{z-4}$ ion) and differences in hydration of the metal-ion complex and bare metal ion (see discussions in Chapters 14 and 15). Most ions that deviate furthest from the line can be identified as having large radii (Pb^{2+}) and the differences are thought to result from this factor and the difference in the number and nature of water molecules occupied on the bare metal cation and on the complex ion. (see Chapter 15).

Similar plots were prepared for comparison of both the volume and heat capacity changes associated with complexation. These comparisons are presented in Figures 17.2 and 17.3, respectively. Absolute heat capacity and volume estimates for H^+(aq) were taken from ABRAHAM and MARCUS (1986) [$\bar{C}_{p,abs}(H^+, aq) = -71$ J $K^{-1}mol^{-1}$] and MILLERO (1972) [$\bar{V}^{abs}(H^+, aq) = -5.4$ cm^3mol^{-1}]. In all cases the properties of bulk water can account for the observed differences in each plot.

All ΔY values (entropies, volumes, and heat capacities) are large because of the displacement of water molecules from the primary hydration spheres of the metal cations. Complexes formed with the weak alkali metals have lower changes presumably because of the increased retention of primary hydration sphere water molecules, and also because of the increased looseness of the EDTA molecule (compared to EDTA when complexed to transition metals) that may lead to decreases in both the volumes and heat capacity changes because of normal electrostatic interactions.

The results in these latter two figures suggest that the volume and heat capacity changes associated with complexation of the majority of monatomic metal cations with EDTA can be reasonably well predicted from linear equations to within 5 cm^3mol^{-1} and 40 J $K^{-1}mol^{-1}$, respectively (although most of the ions are predicted to within 3 cm^3mol^{-1} and 20 J $K^{-1}mol^{-1}$, respectively). These deviations are

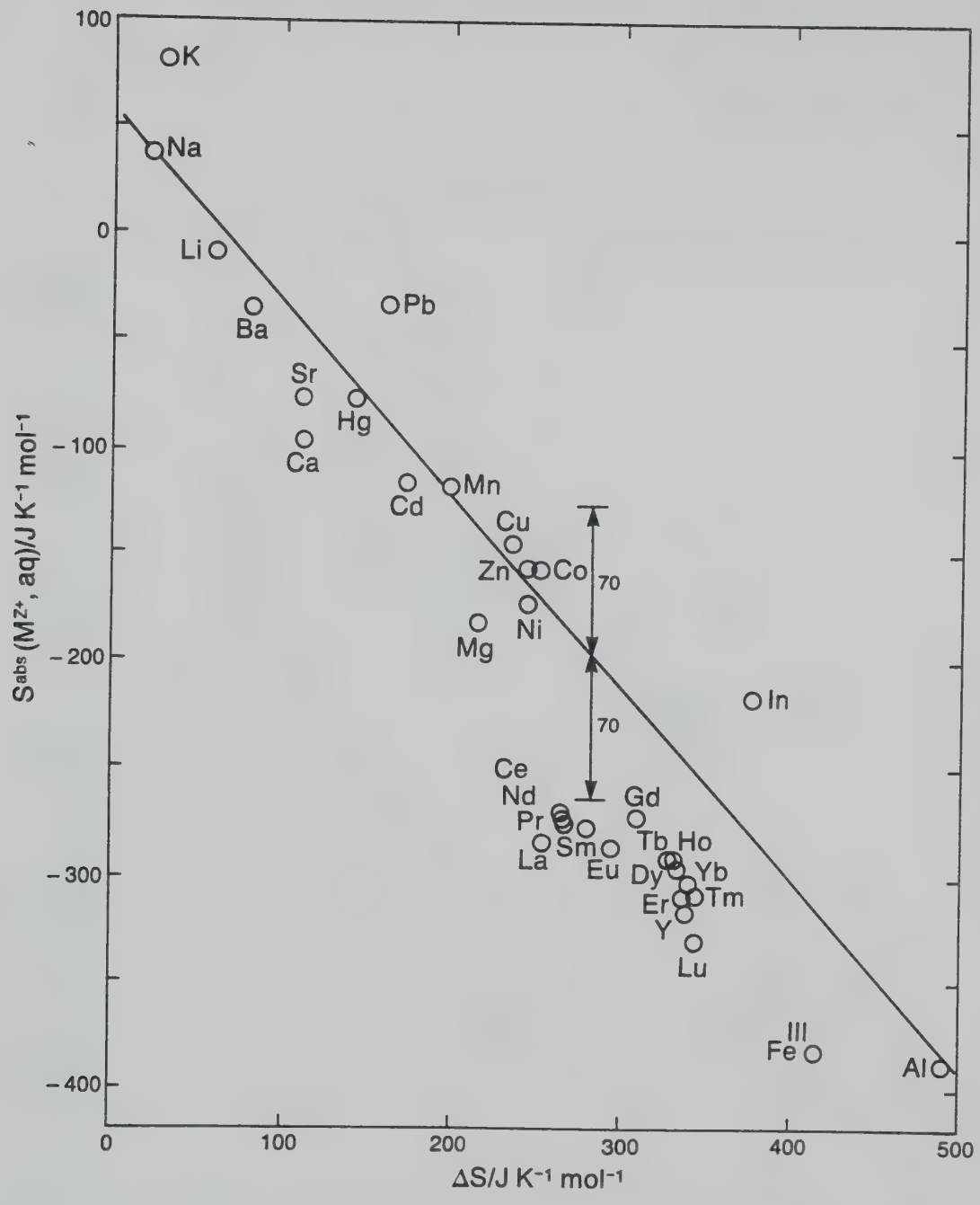

Figure 17.1: $\bar{S}^{abs}(M^{z+})$ plotted against $\Delta S^{\dagger}$ for complexation by $EDTA^{4-}$ by selected metal ions listed in Table 17.2 and several others.

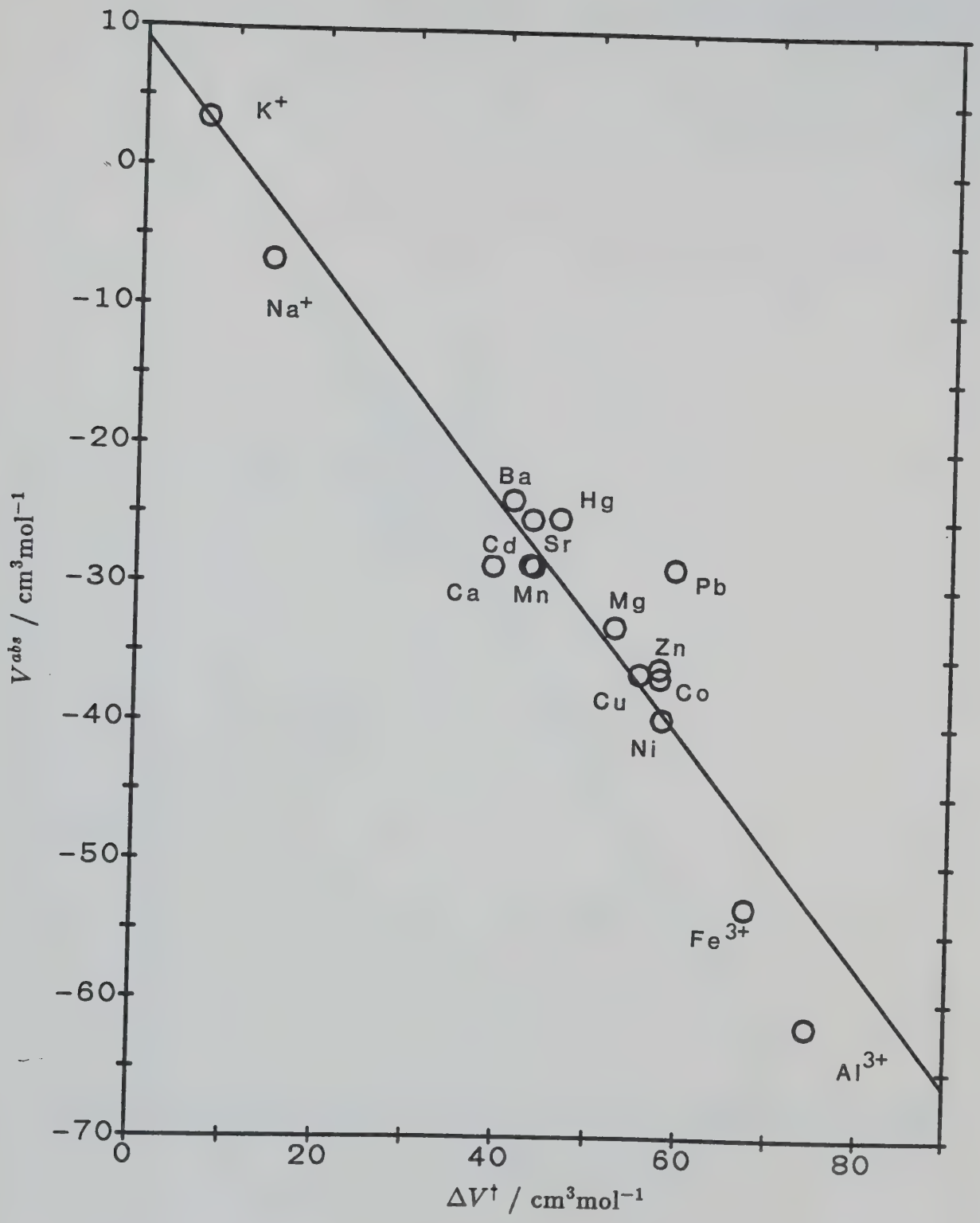

Figure 17.2: $\bar{V}^{abs}(M^{z+})$ plotted against $\Delta\bar{V}^{\dagger}$ for complexation by $EDTA^{4-}$ by selected metal ions listed in Table 17.2.

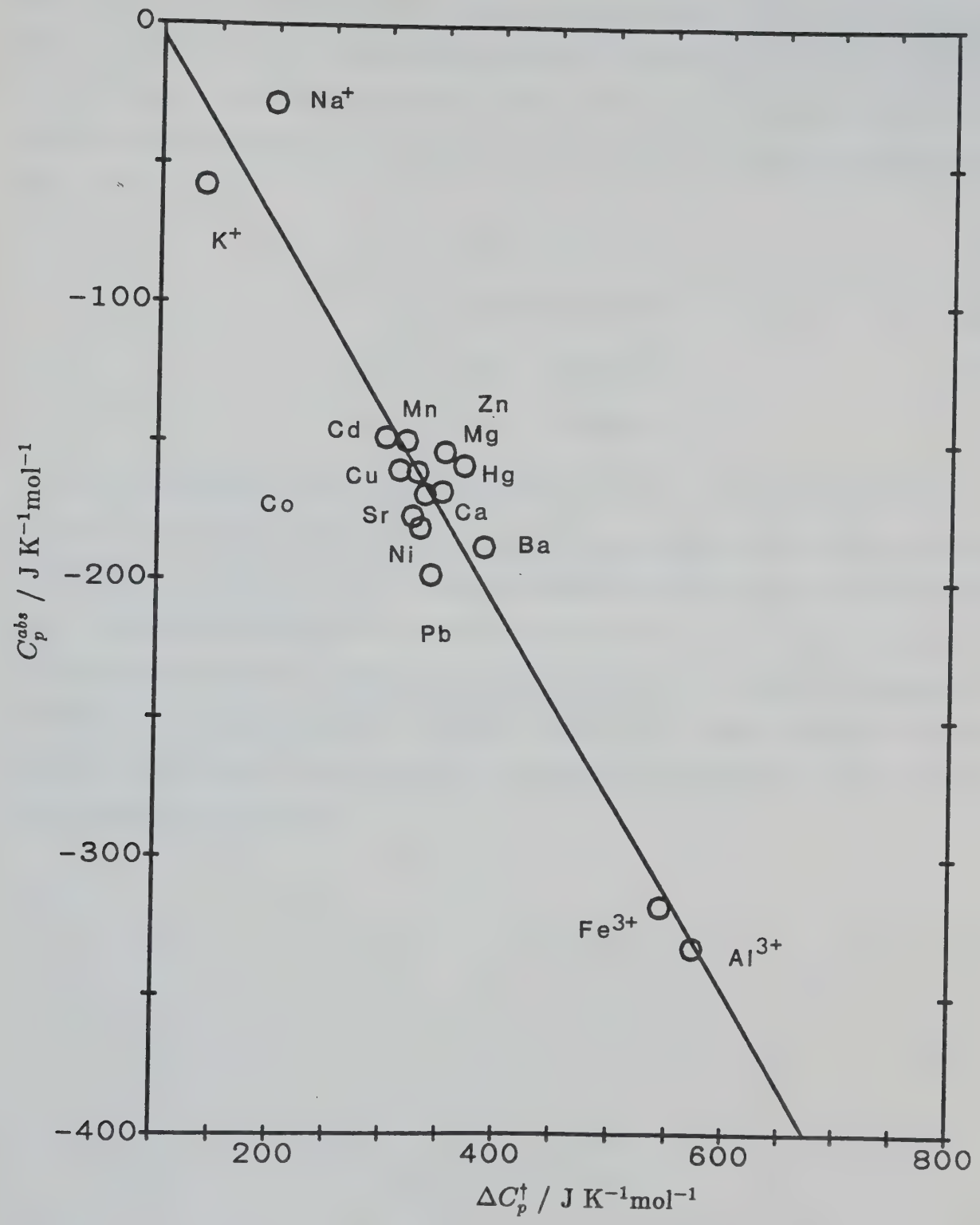

Figure 17.3: $\bar{C}_p^{abs}(M^{z+})$ plotted against $\Delta\bar{C}_p^{\dagger}$ for complexation by $EDTA^{4-}$ by selected metal ions listed in Table 17.2.

slightly worse than estimates of total uncertainties in values obtained by way of direct calorimetric and densimetric results (Chapters 14-16; HOVEY and TREMAINE, 1985). Marginally better relationships are found between the absolute properties of the metal ions and the standard state (infinite dilution) change due to EDTA complexation. The equations that result from all of these calculations are summarized below.

$$V^{abs} = 9.07 - 0.8347\Delta V^{\dagger} \tag{17.8}$$

$$V^{abs} = 11.90 - 0.8097\Delta V^{\circ} \tag{17.9}$$

$$C_p^{abs} = 64.10 - 0.6872\Delta C_p^{\dagger} \tag{17.10}$$

$$C_p^{abs} = 114.31 - 0.6809\Delta C_p^{\circ} \tag{17.11}$$

The heat capacity changes associated with metal-ion complexation reactions can be used to calculate high temperature equilibrium properties for various metal-ion exchange reactions (that can be written isocoulombically) so long as accurate equilibrium constants and enthalpies of reaction are known at some reference temperature (Chapters 14 through 16). The present approach appears to entirely adequate for the prediction of heat capacities for "missing" complex ions. These quantities could then be used in these types of calculations or for interim evaluations of "best" enthalpies of reaction as discussed here.

17.5 References

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Chapter 18

Critical evaluation of conventional ionic standard state heat capacities for aqueous inorganic species at 25°C obtained by way of modern calorimetric measurements.

18.1 Introduction

Heat capacities of aqueous electrolytes are useful in many applications of classical thermodynamic calculations (such as those described in most of the preceding Chapters) and also for some non-classical treatments directed at the solvation of ions. The advent of heat capacity flow microcalorimetry (PICKER *et al.*, 1971) led to many measurements of heat capacities of solutions, especially aqueous solutions containing totally or partially dissociated solutes. Accurate measurements obtained as a function of ionic strength have led to evaluation of standard state heat capacities (infinite dilution) for numerous aqueous electrolytes.

Standard state properties, because they pertain to an infinitely dilute solution, result totally from solute-solvent interactions (consult early discussions in Chapter 2). These interactions have been the subject of several comprehensive works [see, for example, "Solute-solvent Interactions" edited by COETZEE and RITCHIE (1969), or the works of FRANK and WEN (1957) and FRANK and EVANS (1945)]. More recently, much work on solute-solvent interactions has been done in the gas phase where discrete numbers of solvent molecules can be placed on ions, thereby providing valuable thermodynamic information that can be used to elucidate the interactions of ions with solvent molecules in primary solvation spheres in solution [see for example KEBARLE (1977) and MEOT-NER (1987)]. Results of these studies will undoubtedly be essential for the development of rigorous theories for ionic solvation. Heat capacities of gaseous ions are presently inaccessible by direct experimental work be-

cause of uncertainties in $(d^2 \ln K/dT^2)$ calculations involving equilibrium constants obtained over a range of temperatures. Heat capacities of gaseous monatomic ions can be calculated by considering translational degrees of freedom and more complex ions also can be calculated considering more types of molecular motion (MARCUS, private communication). The critically evaluated heat capacities presented in this Chapter can be used to test theories of ionic solvation, and also for more classical calculations regarding the temperature dependences of enthalpies, entropies, Gibbs free energies or equilibrium constants.

18.2 Selections of data

The most recent comprehensive review of the heat capacities of aqueous solutes is the excellent work by PARKER (1965). Most studies that have led to the determination of aqueous solutes in water to 1978 have been listed by SMITH-MAGOWAN and GOLDBERG (1979). At present there is no comprehensive listing of critically evaluated heat capacities for aqueous inorganic ions.

Because of the number of studies that have been carried out over the past few years, primarily only the measurements obtained by using flow calorimeters (at room temperature) need be considered. Results from batch calorimetric measurements are generally a factor of ten less reliable upon extrapolation to infinite dilution than are the results obtained from flow calorimetry. Instead of presenting a comprehensive review that would involve listing all such data and then giving these batch calorimetric results negligible weight with respect to results from flow calorimetry, most of the batch results have not been listed. Results obtained by way of the temperature dependence of enthalpies were not included for similar reasons although in certain cases these data may provide better estimates of standard state heat capacities than those obtained by way of direct heat capacity measurements because of "chemical relaxation" effects (Chapter 4). Another reason for only considering the more modern data presently available is the knowledge of the comprehensive review being prepared that considers heat capacities of all aqueous solutes (by appropriate direct and indirect methods).[1]

[1] L.G. Hepler, private communication.

Because of the direction of the present thesis, the heat capacities of aqueous inorganic ions were more rigorously pursued than those for organic ions. The following listings largely for inorganic ions are considered nearly complete. The results of heat capacity measurements by several workers are presented in Table 18.1. In many cases the original data required some form of recalculation. In most cases these recalculations were done by the present author except that in some cases (sodium carbonate, sodium bicarbonate) these calculations were done by other authors listed in the same grouping for that species in Table 18.1.

There are several studies that have led to standard state heat capacities for a variety of organic ions that were not included in Table 18.1. Only a few organic compounds have been studied by more than one group, hence not much of a critical evaluation can be made. Some pertinent references that report many of the most common organic electrolytes are: PHILIP and DESNOYERS (1972), JOLICOEUR *et al.* (1972, 1975), JOLICOEUR and BOILEAU (1974), FRENCH and CRISS (1982), CARON *et al.* (1985) DEARDON and WOOLLEY (1987), MUSBALLY *et al.* (1976), MAKHATADZE and PRIVALOV (1988), ALLRED and WOOLLEY (1981b), DESNOYERS *et al.* (1976), LEDUC and DESNOYERS (1973), Chapters 14 through 16, PERRON and DESNOYERS (1979), DESNOYERS *et al.* (1973), SWAY *et al.* (1973), OSTIGUY *et al.* (1977), CARON *et al.* (1985), CABANI *et al.* (1973), KIYOHARA *et al.* (1975a, b), HALLÉN *et al.* (1986), OLOFSSON *et al.* (1984), HOVEY and TREMAINE (1985).

18.3 Critical evaluation of results

Standard state heat capacities of electrolytes can be converted into conventional ionic values for ions by using the convention $\bar{C}_p^\circ(H^+, aq) \equiv 0$. Conventional ionic heat capacities for strong acids are therefore equal to the "best" values for the electrolyte. Because anions and cations appear in a variety of different electrolytes, initial choices for important ions must be consistent with the best data for electrolytes containing these ions.

In the present scheme, the heat capacities of especially well behaved electrolytes (high purity, no chemical handling or storage problems), or results from several different studies that were in very good agreement, were used in initial selections of

Table 18.1: Listing of modern experimental determinations of heat capacities of aqueous solutions.

Ion of interest	Electrolyte	$\bar{C}_p^\circ$	Reference
H^+	definition	0	
Li^+	LiCl	−65.2	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	LiBr	−69.1	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	LiCl	−65.4‡	GUCKER and SCHMINKE (1932)
Na^+	NaF	−74.9	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	NaCl	−84.4	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	NaBr	−88.1	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	NaI	−76.5	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	NaCl	−84.6	SINGH *et al.* (1976)
	NaBr	−88.4	SINGH *et al.* (1976)
	NaCl	−83.7	ALLRED and WOOLLEY (1981*a*)
	$NaClO_4$	15.2	SINGH *et al.* (1976)
	$NaClO_4$	16.6	ROUX *et al.* (1978)
	$NaClO_3$	−16.8	ROUX *et al.* (1978)
	$NaNO_3$	−29	ROUX *et al.* (1978)
	$NaBrO_3$	−50.5	ROUX *et al.* (1978)
	$NaIO_3$	−34.	ROUX *et al.* (1978)
	$NaIO_3$	−29.6	SPITZER *et al.* (1979)
	$NaNO_3$	−28.9	ENEA *et al.* (1977)
	NaI	−77	SALUJA *et al.* (1986)
	$NaIO_3$	−32	SALUJA *et al.* (1986)
	NaCl	−85.5	PERRON *et al.* (1981)
	NaCl	84.3	OLOFSSON (1979)
K^+	KF	−104.0	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	KCl	−114.2	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	KBr	−118.3	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)

Table 18.1: continued.

Ion of interest	Electrolyte	$\bar{C}_p^\circ$	Reference
	KI	−108.7	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	KCl	−114.1	SINGH *et al.* (1976)
	KBr	−119.1	SINGH *et al.* (1976)
	KIO_3	−59.0	SALUJA *et al.* (1986)
	$KClO_4$	−15.0	SALUJA *et al.* (1986)
	KCl	−116.1	OLOFSSON *et al.* (1979)
	KNO_3	−59.4	OLOFSSON *et al.* (1979)
	$KClO_3$	−42.5	ROUX *et al.* (1978)
	$KBrO_3$	−77.3	ROUX *et al.* (1978)
	KIO_3	−58.7	ROUX *et al.* (1978)
Rb^+	RbF	−124.9	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	RbCl	−135.9	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	RbBr	−139.0	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	RbI	−131.5	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
Cs^+	CsF	−136.3	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	CsCl	−148.9	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	CsBr	−155.3	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	CsI	−145.0	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	CsF	−140	SALUJA *et al.* (1986)
	CsCl	−149	SALUJA *et al.* (1986)
	CsI	−145	SALUJA *et al.* (1986)
	$CsIO_3$	−101	SALUJA *et al.* (1986)
Mg^{2+}	$MgCl_2$	−268.6	DESNOYERS *et al.* (1976)
			PERRON *et al.* (1974)
	$Mg(NO_3)_2$	−160.1	SPITZER *et al.* (1979)
	$Mg(ClO_4)_2$	−65.7	SPITZER *et al.* (1978)

Table 18.1: continued.

Ion of interest	Electrolyte	$\bar{C}_p^\circ$	Reference
	$MgCl_2$	−252.5	PERRON *et al.* (1981)
	$Mg(NO_3)_2$	−165.7‡	DRAKIN *et al.* (1967)
Ca^{2+}	$CaCl_2$	−281.5	DESNOYERS *et al.* (1976)
			PERRON *et al.* (1974)
	$Ca(NO_3)_2$	−170.0	SPITZER *et al.* (1979)
	$CaCl_2$	−282.0	SPITZER *et al.* (1978)
	$Ca(ClO_4)_2$	−76.8	SPITZER *et al.* (1978)
	$CaCl_2$	−278.3	PERRON *et al.* (1981)
	$CaCl_2$	−272‡	KARAPET'YANTS *et al.* (1970)
Sr^{2+}	$SrCl_2$	−289.2	DESNOYERS *et al.* (1976)
			PERRON *et al.* (1974)
	$SrCl_2$	−281‡	KARAPET'YANTS *et al.* (1970)
Ba^{2+}	$BaCl_2$	−300.0	DESNOYERS *et al.* (1976)
			PERRON *et al.* (1974)
	$BaCl_2$	−311.1	WHITE *et al.* (1936)
Sc^{3+}	$Sc(ClO_4)_3$	−146 †‡	BABAKULOV *et al.* (1974)
Cr^{3+}	$Cr(NO_3)_3$	−240	SPITZER *et al.* (1979)
	$Cr(NO_3)_3$	−364‡	MYASNIKOVA *et al.* (1968)
Mn^{2+}	$Mn(ClO_4)_2$	−61.7	SPITZER *et al.* (1978)
	$Mn(NO_3)_2$	−156.0	SPITZER *et al.* (1979)
	$MnCl_2$	−259.3	SPITZER *et al.* (1979)
	$Mn(NO_3)_2$	−199.2‡	DRAKIN *et al.* (1967)
Fe^{3+}	$Fe(ClO_4)_3$	−151.5	Chapter 9
	$Fe(ClO_4)_3$	−159.9	Chapter 9
	$Fe(NO_3)_3$	−402‡	MYASNIKOVA *et al.* (1968)
Fe^{2+}	$FeCl_2$	−289‡	KARAPET'YANTS*et al.* (1977)
	$Fe(ClO_4)_2$	−76.8	Chapter 9
Co^{2+}	$Co(ClO_4)_2$	−81.0	SPITZER *et al.* (1978)
	$Co(NO_3)_2$	−170.2	SPITZER *et al.* (1979)

Table 18.1: continued.

Ion of interest	Electrolyte	$\bar{C}_p^\circ$	Reference
	$CoCl_2$	−278.7	SPITZER *et al.* (1978)
	$CoCl_2$	−278.2‡	MISHCHENKO and PODGORNAYA (1961)
Ni^{2+}	$Ni(ClO_4)_2$	−93.1	SPITZER *et al.* (1978)
	$NiCl_2$	−294.0	SPITZER *et al.* (1978)
	$Ni(NO_3)_2$	−186.5	SPITZER *et al.* (1979)
	$NiCl_2$	−295.2	PERRON *et al.* (1981)
Cu^{2+}	$Cu(ClO_4)_2$	−72.4	SPITZER *et al.* (1978)
	$CuNO_3)_2$	−161.2	SPITZER *et al.* (1979)
	$CuCl_2$	−28.0‡	VASILËV *et al.*1974)
Zn^{2+}	$Zn(ClO_4)_2$	−73.1	SPITZER *et al.* (1978)
	$Zn(NO_3)_2$	−165.3	SPITZER *et al.* (1979)
	$Zn(NO_3)_2$	−186.6‡	DRAKIN *et al.* (1967)
Y^{3+}	$Y(ClO_4)_3$	−139†‡	BABAKULOV *et al.* (1974)
	YCl_3	−418	KARAPET'YANTS *et al.* (1976)
Ag^{+}	$AgNO_3$	−36.8	SINGH *et al.* (1978)
	$AgClO_4$	11.0	SINGH *et al.* (1978)
Cd^{2+}	$Cd(ClO_4)_2$	−57.4	SPITZER *et al.* (1978)
	$Cd(NO_3)_2$	−152.3	SPITZER *et al.* (1978)
	$Cd(NO_3)_2$	−223.8‡	DRAKIN *et al.* (1967)
Hg^{2+}	$Hg(ClO_4)_2$	−67.3	Chapter 3
Pb^{2+}	$Pb(ClO_4)_2$	−107.0	Chapter 3
	$Pb(NO_3)_2$	−225.9‡	DRAKIN *et al.* (1967)
La^{3+}	$La(ClO_4)_3$	−211.7†	SPEDDING *et al.* (1975)
	$LaCl_3$	−492.9†	SPEDDING and JONES (1966)
	$La(NO_3)_3$	−316.6†	SPEDDING *et al.* (1979)
	$LaCl_3$	−464	SPITZER *et al.* (1979)
	$La(NO_3)_3$	−682‡	MYASNIKOVA *et al.* (1968)
	$La(ClO_4)_3$	−218†‡	BABAKULOV *et al.* (1974)

Table 18.1: continued.

Ion of interest	Electrolyte	$\bar{C}_p^\circ$	Reference
Ce^{3+}	$CeCl_3$	−466‡	VASIL'EV *et al.* (1975)
	$Ce(NO_3)_3$	−548‡	Myasnikova *et al.* (1968)
Pr^{3+}	$Pr(ClO_4)_3$	−232.6†	SPEDDING *et al.* (1975)
	$PrCl_3$	−500.0†	SPEDDING *et al.* (1975)
	$Pr(NO_3)_3$	−317.4†	SPEDDING *et al.* (1979)
Nd^{3+}	$Nd(ClO_4)_3$	−223.0†	SPEDDING *et al.* (1975)
	$NdCl_3$	−488.7†	SPEDDING and JONES (1966)
	$NdNO_3)_3$	−302.5†	SPEDDING *et al.* (1979)
Sm^{3+}	$Sm(ClO_4)_3$	−217.1†	SPEDDING *et al.* (1975)
	$SmCl_3$	−489.1†	SPEDDING *et al.* (1975)
	$Sm(NO_3)_3$	−293.2†	SPEDDING *et al.* (1979)
Eu^{3+}	$Eu(ClO_4)_3$	−195.0†	SPEDDING *et al.* (1975)
	$EuCl_3$	−461.08†	SPEDDING *et al.* (1975)
Gd^{3+}	$Gd(ClO_4)_3$	−189.1†	SPEDDING *et al.* (1975)
	$GdCl_3$	−473.6†	SPEDDING *et al.* (1975)
	$Gd(NO_3)_3$	−282.7†	SPEDDING *et al.* (1979)
Tb^{3+}	$Tb(ClO_4)_3$	−187.4†	SPEDDING *et al.* (1975)
	$TbCl_3$	−454.0†	SPEDDING *et al.* (1975)
	$Tb(NO_3)_3$	−295.3†	SPEDDING *et al.* (1979)
Dy^{3+}	$Dy(ClO_4)_3$	−174.9†	SPEDDING *et al.* (1975)
	$DyCl_3$	−451.0†	SPEDDING and JONES (1966)
	$Dy(NO_3)_3$	−292.09†	SPEDDING *et al.* (1979)
Ho^{3+}	$Ho(ClO_4)_3$	−175.7†	SPEDDING *et al.* (1975)
	$HoCl_3$	−457.3†	SPEDDING *et al.* (1975)
	$Ho(NO_3)_3$	−302.0†	SPEDDING *et al.* (1979)
Er^{3+}	$Er(ClO_4)_3$	−182.4†	SPEDDING *et al.* (1975)
	$ErCl_3$	−452.7†	SPEDDING and JONES (1966)
	$Er(NO_3)_3$	−311.0†	SPEDDING *et al.* (1979)

Table 18.1: continued.

Ion of interest	Electrolyte	$\bar{C}_p^\circ$	Reference
Tm^{3+}	$Tm(ClO_4)_3$	−172.4†	SPEDDING *et al.* (1975)
	$TmCl_3$	−446.0†	SPEDDING *et al.* (1975)
	$Tm(NO_3)_3$	−307.3†	SPEDDING *et al.* (1979)
Yb^{3+}	$Yb(ClO_4)_3$	−195.8†	SPEDDING *et al.* (1975)
	$YbCl_3$	−448.9†	SPEDDING and JONES (1966)
	$Yb(NO_3)_3$	−307.8†	SPEDDING *et al.* (1979)
Lu^{3+}	$Lu(ClO_4)_3$	−182.8†	SPEDDING *et al.* (1975)
	$LuCl_3$	−448.9†	SPEDDING *et al.* (1975)
	$Lu(NO_3)_3$	−315.3†	SPEDDING *et al.* (1979)
Al^{3+}	$AlCl_3$	−583.3	Chapter 6
	$Al(NO_3)_3$	−335.3	Chapter 6
	$Al(ClO_4)_3$	−221 †‡	BABAKULOV *et al.* (1974)
	$Al(NO_3)_3$	−364‡	MYASNIKOVA *et al.* (1968)
Ga^{3+}	$Ga(ClO_4)_3$	−146 †‡	BABAKULOV *et al.* (1974)
In^{3+}	$In(ClO_4)_3$	−204 †‡	BABAKULOV *et al.* (1974)
UO_2^{2+}	$UO_2(ClO_4)_2$	−8.66	Chapter 11
	UO_2Cl_2	−227 †‡	KAPUSTINSKY and LIPILINA(1955)
NH_4^+	NH_4Cl	−55.6	ROUX *et al.* (1978)
	NH_4ClO_4	47.2	ROUX *et al.* (1978)
	NH_4NO_3	−1.2	ROUX *et al.* (1978)
	NH_4NO_3	−3.0	ROUX *et al.* (1978)
	NH_4Cl	−56.4	ALLRED and WOOLLEY (1981*b*)
	NH_4Cl	−56.6	DESNOYERS *et al.* (1976)
			LEDUC and DESNOYERS *et al.* (1973)
	NH_4Br	−66.9	DESNOYERS *et al.* (1976)
			LEDUC and DESNOYERS *et al.* (1973)

Table 18.1: continued.

Ion of interest	Electrolyte	$\bar{C}_p^\circ$	Reference
Me_4N^+	Me_4NBr	109.0	PHILIP and DESNOYERS (1972)
	Me_4NBr	106.3	PERRON *et al.* (1976)
	Me_4NCl	107.7	PERRON *et al.* (1976)
	Me_4NI	117.2	PERRON *et al.* (1976)
Et_4N^+	Et_4NCl	388.6	PERRON *et al.* (1976)
	Et_4NBr	381.4	PERRON *et al.* (1976)
	Et_4NI	391.8	PERRON *et al.* (1976)
	Et_4NBr	388.0	PHILIP and DESNOYERS (1972)
Pr_4N^+	Pr_4NCl	795.8	PERRON *et al.* (1976)
	Pr_4NBr	789.0	PERRON *et al.* (1976)
	Pr_4NI	803.5	PERRON *et al.* (1976)
	Pr_4NBr	789.4	PHILIP and DESNOYERS (1972)
Bu_4N^+	Bu_4NCl	1208.7	PERRON *et al.* (1976)
	Bu_4NBr	1208.0	PERRON *et al.* (1976)
	Bu_4NI	1218.3	PERRON *et al.* (1976)
	Bu_4NBr	1209.6	PHILIP and DESNOYERS (1972)
	Bu_4NBr	1210	PHILIP and DESNOYERS (1972)
	Bu_4NBr	1209.6	PERRON *et al.* (1976)
Et_4N^+	Et_4NBr	388.0	PERRON *et al.* (1976)
$n-Bu_4P^+$	$n-Bu_4PCl$	1289	WAKABAYASHI *et al.* (1986)
	$n-Bu_4PBr$	1251	JOLICOEUR and PHILIP (1975)
$n-Bu_3PhP^+$	$n-Bu_3PhPCl$	1244	WAKABAYASHI *et al.* (1986)
$n-Bu_2Ph_2P^+$	$n-Bu_2Ph_2PCl$	1198	WAKABAYASHI *et al.* (1986)
$n-BuPh_3P^+$	$n-BuPh_3PCl$	1139	WAKABAYASHI *et al.* (1986)

Table 18.1: continued.

Ion of interest	Electrolyte	$\bar{C}_p^\circ$	Reference
Ph_4P^+	Ph_4PBr	1090	JOLICOEUR andPHILIP (1975)
	Ph_4PCl	1198	WAKABAYASHI *et al.* (1986)
Cl^-	HCl	−126.6	TREMAINE *et al.* (1986)
	HCl	−127.0	DESNOYERS *et al.* (1976)
			FORTIER *et al.* (1974)
	HCl	−127.2	SINGH *et al.* (1976)
	HCl	−124.7	ALLRED and WOOLLEY (1981*a*)
	HCl	−125	SALUJA *et al.* (1986)
	HCl	−122.2‡	GUCKER and SCHMINKE (1932)
Br^-	HBr	−132.6	SINGH *et al.* (1976)
OH^-	NaOH	−94.6	DESNOYERS *et al.* (1976)
			PERRON *et al.* (1975)
	NaOH	−97.40	ROUX *et al.* (1984)
	NaOH	−100.5	ALLRED and WOOLLEY (1981*a*)
	NaOH	−96.2	SINGH *et al.* (1976)
	KOH	−130.52	ROUX *et al.* (1984)
	KOH	−127.0	SINGH *et al.* (1976)
	KOH	−134.3‡	GUCKER and SCHMINKE (1932)
	LiOH	−77.87	ROUX *et al.* (1984)
IO_3^-	$NaIO_3$	−34.0	ROUX *et al.* (1978)
	$NaIO_3$	−29.6	SPITZER *et al.* (1979)
	KIO_3	−58.7	ROUX *et al.* (1978)
	KIO_3	−59	SALUJA *et al.* (1986)
	$CsIO_3$	−101	SALUJA *et al.* (1986)
BrO_3^-	$KBrO_3$	−77.3	ROUX *et al.* (1978)
	$NaBrO_3$	−50.5	ROUX *et al.* (1978)
ClO_3^-	$KClO_3$	−42.5	ROUX *et al.* (1978)
	$NaClO_3$	−16.8	ROUX *et al.* (1978)
ClO_4^-	$HClO_4$	−27.1	SINGH *et al.* (1977)
	$HClO_4$	−25.5	Chapter 2

Table 18.1: continued.

Ion of interest	Electrolyte	$\bar{C}_p^\circ$	Reference
NO_3^-	HNO_3	−72.1	ENEA *et al.* (1977)
	HNO_3	−71.6	Chapter 2
HS^-	NaHS	−51	BARBERO *et al.* (1982)
SO_4^{2-}	Na_2SO_4	−191.7	DESNOYERS *et al.* (1976)
			PERRON *et al.* (1975)
	K_2SO_4	−254.5	DESNOYERS *et al.* (1976)
			PERRON *et al.* (1975)
	K_2SO_4	−256.7	Chapter 2
	K_2SO_4	−251.0	OLOFSSON *et al.* (1978)
	Na_2SO_4	−190.1	OLOFSSON *et al.* (1978)
HSO_4^-	$H^+ + HSO_4^-$	−27.2(21.7)†	LARSON *et al.* (1982)
		−16.5	Chapter 4
HSO_3^-	$NaHSO_3$	34.0	BARBERO *et al.* (1983)
	$NaHSO_3$	41.2	ALLRED *et al.* (1981)
	$KHSO_3$	1.4	BARBERO *et al.* (1983)
SO_3^{2-}	Na_2SO_3	−177.8	ALLRED *et al.* (1981)
$S_2O_3^{2-}$	$Na_2S_2O_3$	−163.6	OLOFSSON *et al.* (1978)
$S_2O_8^{2-}$	$Na_2S_2O_8$	−29.3	OLOFSSON *et al.* (1978)
	$K_2S_2O_8$	−84.0	OLOFSSON *et al.* (1978)
CO_3^{2-}	Na_2CO_3	−179.3	DESNOYERS *et al.* (1976)
			PERRON *et al.* (1975)
	Na_2CO_3	−215.5	LARSON *et al.* (1982)
HCO_3^-	$NaHCO_3$	−7.2 † (−8.7)	DESNOYERS *et al.* (1976)
			PERRON *et al.* (1975)
	$NaHCO_3$	−11.6	LARSON *et al.* (1982)
	$NaHCO_3$	−2.6 † (−4.1)	BARBERO *et al.* (1983)
	$KHCO_3$	−38.5 † (−40.0)	BARBERO *et al.* (1983)

Table 18.1: continued.

Ion of interest	Electrolyte	$\bar{C}_p^\circ$	Reference
PO_4^{3-}	Na_3PO_4	−367	LARSON *et al.* (1982)
HPO_4^{2-}	Na_2HPO_4	−168.1	LARSON *et al.* (1982)
$H_2PO_4^-$	NaH_2PO_4	8.6	LARSON *et al.* (1982)
$H_3PO_4^\circ$	H_3PO_4	94.5	LARSON *et al.* (1982)
$Fe(CN)_6^{3-}$	$K_3Fe(CN)_6$	−218.7	SPITZER *et al.* (1979)
$Fe(CN)_6^{4-}$	$K_4Fe(CN)_6$	−481	SPITZER *et al.* (1979)
$Al(OH)_4^-$	$NaAl(OH)_4$	138.7	Chapter 7
$B(OH)_4^-$	$NaB(OH)_4$	31.8	Chapter 8
MnO_4^-	$KMnO_4$	1.5	SPITZER *et al.*](1979)
CrO_4^{2-}	K_2CrO_4	−245.9	Chapter 5
	K_2CrO_4	−241.8	Chapter 5
	K_2CrO_4	−245.2	Chapter 5
	K_2CrO_4	−239.5	OLOFFSON *et al.* (1978) (Chapter 5)
	K_2CrO_4	−233.2‡	VASILEV *et al.* (1984) (Chapter 5)
$HCrO_4^-$	$K^+ + HCrO_4^-$	14.7	Chapter 5
$Cr_2O_7^{2-}$	$2K^+ + Cr_2O_7^{2-}$	−105.0	Chapter 5
MoO_4^{2-}	Na_2MoO_4	−122.8	OLOFFSON *et al.* (1978)
WO_4^{2-}	Na_2WO_4	−110.4	OLOFFSON *et al.* (1978)
OAc^-	NH_4OAc	102.6	DESNOYERS *et al.* (1976) LEDUC and DESNOYERS (1973)
	NaOAc	67.8	DESNOYERS *et al.* (1976) LEDUC and DESNOYERS (1973)
	NaOAc	67.7	ALLRED and WOOLLEY (1981*b*)

Table 18.1: continued.

Ion of interest	Electrolyte	$\bar{C}_p^\circ$	Reference
BPh_4^-	$NaBPh_4$	1113.4	DESNOYERS *et al.* (1976) JOLICOEUR *et al.* (1972)
ReO_4^-	$NaReO_4$	36.8	AHLUWALIA and COBBLE (1964)
	$HReO_4$	−13.3	AHLUWALIA and COBBLE (1964)
	Selected inorganic neutral solutes		
CO_2	CO_2	243.2	BARBERO *et al.* (1983)
SO_2	SO_2	195	BARBERO *et al.* (1983)
HIO_3°	HIO_3°	−40	WOOLLEY and HEPLER (1977)
$MgSO_4$	$MgSO_4$	168	WOOLLEY and HEPLER (1977)
UO_2SO_4	UO_2SO_4	−70.4	Chapter 12
H_2S	H_2S	178.5	BARBERO *et al.* (1982)
$B(OH)_3$	$B(OH)_3$	107.4	Chapter 8

† These values were recalculated using extended Debye-Hückel equations that were derived in Chapter 4 (all data from Spedding *et al.* were refit using this treatment). Values that appear in parentheses indicate recalculations taking into account "chemical relaxation" (or improved accounts of chemical relaxation).

‡ These values were derived from results obtained by batch calorimetric measurements and are all less reliable than the other values listed in the Table.

the most important ions required for calculations of other ionic species. For the well behaved acidic electrolytes, hydrochloric, perchloric, and nitric, these precise values were selected for the conventional ionic values of chloride, nitrate, and perchlorate ions. The general averaging scheme that was employed here and for other solutes listed in Table 18.1 involved weighting of the listed values in accord with our estimates of uncertainties in the respective values, and in accord with the self-consistency of results available for a single electrolyte (i.e. for Na^+, the self-consistency of values for NaCl, $NaClO_4$, etc.).

The weighted averages of the data were done considering the following generalizations: the results of ALLRED and WOOLLEY (1981) were not included in any of the averages because of regular (but small) differences between their results and other reliable results; the results from DESNOYERS and colleagues were weighted twice that for most other results because of the larger data sets employed by these authors and our estimates of reliability; other results from HEPLER and co-workers and results from the present thesis were given a weight of one corresponding to our belief that these data are of the same accuracy as the "best" measurements but since normally only one half of the data points were obtained for similar electrolytes compared with results from DESNOYERS and colleagues, this weighting seemed appropriate; in cases where values calculated for individual ions were approximately within our estimates of expected differences among researchers ($\pm$ 3 J $K^{-1}mol^{-1}$) except for one extraneous value, this latter value was ignored (most often these data are traceable to chemical difficulties); results from electrolytes that are classically ill-behaved were weighted less than for other results (chemical problems); results for electrolytes containing metal ions were given a weighting in accord with expectations regarding the possibility of ion pair formation-that is, results of metal perchlorate salts were weighted more heavily than results for nitrate or chloride salts.

All of the critically evaluated selections are cited in Table 18.2. The accuracies of the selected properties are divided into three categories depending on the listing in the table. For ions believed to be the most accurate ($\pm$ 1 J $K^{-1}mol^{-1}$) the recommended values are quoted to one decimal place, values of normal accuracy ($\pm$ 2-5 J $K^{-1}mol^{-1}$) are quoted to the nearest J $K^{-1}mol^{-1}$, and values that have higher uncertainties are listed along with our estimates of probable uncertainties. For some

of these ions derived from batch calorimetric measurements (indicated by ‡ in Table 18.1) the *total* uncertainties may be larger.

All of the values cited in Table 18.2 are considered to be the most reliable presently available. Some results of investigations of the dependence of heat capacities of aqueous solutes on charge, radius, and other structural factors are presented in the following Chapter using these critically selected values.

Table 18.2: Selected conventional $[\bar{Y}(H^+, aq) \equiv 0]$ ionic partial molar heat capacities at 25°C.

Ion	$\bar{C}_p^\circ$	from salt(s)
Li^+	61.8	LiCl, LiBr
Na^+	42.5	HCl
K^+	12.7	KCl
Rb^+	−9.0	RbCl
Cs^+	−23.7	CsCl, CsI, CsBr, CsF
Mg^{2+}	−14.7	$Mg(ClO_4)_2$, $Mg(NO_3)_2$, $MgCl_2$
Ca^{2+}	−25	$Ca(ClO_4)_2$
Sr^{2+}	−35	$SrCl_2$
Ba^{2+}	−46	$BaCl_2$
Sc^{3+}	-68 ± 50	$Sc(ClO_4)_3$
Cr^{3+}	-87 ± 60	$Cr(NO_3)_3$
Mn^{2+}	−10	$Mn(ClO_4)_2$, $Mn(NO_3)_2$
Cr^{3+}	−25	$Cr(NO_3)_3$
Fe^{2+}	−25	$Fe(ClO_4)_2$
Fe^{3+}	-105 ± 15	$Fe(ClO_4)_3$
Co^{2+}	−29	$CO(ClO_4)_2$
Ni^{2+}	−41.6	$Ni(ClO_4)_2$, $Ni(NO_3)_2$, $NiCl_2$
Cu^{2+}	−20	$Cu(ClO_4)_2$, $Cu(NO_3)_2$
Zn^{2+}	−21.4	$Zn(ClO_4)_2$, $Zn(NO_3)_2$
Y^{3+}	-61 ± 50	$Y(ClO_4)_3$
Ag^+	36.0	$AgNO_3$, $AgClO_4$
Cd^{2+}	−6	$Cd(ClO_4)_2$, $Cd(NO_3)_2$
Hg^{2+}	−15	$Hg(ClO_4)_2$
Pb^{2+}	−55	$Pb(ClO_4)_2$
Al^{3+}	−119.3	$AlCl_3$, $Al(NO_3)_3$
Ga^{3+}	-68 ± 50	$Ga(ClO_4)_3$
In^{3+}	-126 ± 50	$In(ClO_4)_3$
Ce^{3+}	−85	$CeCl_3$
La^{3+}	-137 ± 20	$La(ClO_4)_3$, $La(NO_3)_3$
Pr^{3+}	-137 ± 20	$Pr(ClO_4)_3$, $Pr(NO_3)_3$, $PrCl_3$
Nd^{3+}	-125 ± 20	$Nd(ClO_4)_3$, $Nd(NO_3)_3$, $NdCl_3$
Sm^{3+}	-119 ± 25	$Sm(ClO_4)_3$, $Sm(NO_3)_3$, $SmCl_3$
Eu^{3+}	-105 ± 20	$Eu(ClO_4)_3$, $EuCl_3$
Gd^{3+}	-97 ± 20	$Gd(ClO_4)_3$, $Gd(NO_3)_3$, $GdCl_3$
Tb^{3+}	-100 ± 15	$Tb(ClO_4)_3$, $Tb(NO_3)_3$, $TbCl_3$
Dy^{3+}	-90 ± 15	$Dy(ClO_4)_3$, $Dy(NO_3)_3$, $DyCl_3$
Ho^{3+}	-94 ± 15	$Ho(ClO_4)_3$, $Ho(NO_3)_3$, $HoCl_3$
Er^{3+}	-101 ± 10	$Er(ClO_4)_3$, $Er(NO_3)_3$, $ErCl_3$

Table 18.2: continued.

Ion	$\bar{C}_p^\circ$	from salt(s)
Tm^{3+}	-94 ± 20	$Tm(ClO_4)_3$, $Tm(NO_3)_3$, $TmCl_3$
Yb^{3+}	-109 ± 15	$Yb(ClO_4)_3$, $Yb(NO_3)_3$, $YbCl_3$
Lu^{3+}	-103 ± 15	$Lu(ClO_4)_3$, $Lu(NO_3)_3$, $LuCl_3$
UO_2^{2+}	44.4	$UO_2(ClO_4)_2$
NH_4^+	70.2	NH_4Cl, NH_4NO_3 (NH_4ClO_4)
Me_4N^+	236	Me_4NCl, Me_4NBr, Me_4NI
Et_4N^+	515	Et_4NCl, Et_4NBr, Et_4NI
Pr_4N^+	922	Pr_4NCl, Pr_4NBr, Pr_4NI
Bu_4N^+	1338	Bu_4NCl, Bu_4NBr, Bu_4Ni
Cl^-	-126.9	HCl
F^-	-117.0	NaF, KF
Br^-	-131.0	NaBr, KBr (HBr)
I^-	-119.8	NaI, KI
OH^-	-140	NaOH, KOH, LiOH
BrO_3^-	-91.5	$KBrO_3$, $NaBrO_3$
ClO_3^-	-57	$KClO_3$, $NaClO_3$
NO_3^-	-71.8	HNO_3
IO_3^-	-32	$NaIO_3$
ClO_4^-	-26.0	$HClO_4$, $NaClO_4$
HS^-	-94	NaHS
SO_4^{2-}	-280	K_2SO_4, (Na_2SO_4)
HSO_4^-	-19	$H[HSO_4]$
HSO_3^-	-10	$NaHSO_3$, $KHSO_3$
$S_2O_3^{2-}$	-249	$Na_2S_2O_3$
$S_2O_8^{2-}$	-112	$Na_2S_2O_8$, $K_2S_2O_8$
SO_3^{2-}	-263	Na_2SO_3
PO_4^{3-}	-495	Na_3PO_4
HPO_4^{2-}	-253	Na_2HPO_4
$H_2PO_4^-$	-34	NaH_2PO_4
HCO_3^-	-52	$KHCO_3$, $NaHCO_3$
CO_3^{2-}	-300.5	Na_2CO_3
OAc^-	25.3	NaOAc
Oct^-	551	NaOct
BPh_4^-	1070.9	$NaBPh_4$
CrO_4^{2-}	-270	K_2CrO_4
$HCrO_4^-$	2.0	$K_2Cr_2O_7$
$Cr_2O_7^{2-}$	-130	$K_2Cr_2O_7$
MoO_4^{2-}	-207.8	Na_2MoO_4

Table 18.2: continued.

Ion	$\bar{C}_p^\circ$	from salt(s)
WO_4^{2-}	−195.4	Na_2WO_4
ReO_4^-	-10 ± 20	$NaReO_4$, $HReO_4$
$Fe(CN)_6^{3-}$	−256.8	$K_3Fe(CN)_6$
$Fe(CN)_6^{4-}$	−531.8	$K_4Fe(CN)_6$
$Al(OH)_4^-$	96.2	$NaAl(OH)_4$
$B(OH)_4^-$	−10.7	$NaB(OH)_4$
Selected inorganic neutrals		
CO_2	243	
SO_2	195	
CH_3COOH	170	
NH_3	75	
Bu_4NBut	1550	
Bu_4NOct	1910	
$MgSO_4$	−168	
HIO_3	−40	
H_2S	178.5	
$B(OH)_3$	107.4	

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Chapter 19

Semi-empirical relationships involving absolute entropies and heat capacities of aqueous solutes at 25°C

19.1 Introduction

Standard state heat capacities of aqueous species are important fundamental thermodynamic properties. Only recently have many standard state heat capacities for aqueous ions been determined. Because heat capacities for many aqueous species are still unknown and also in certain cases because they will be difficult to measure (chemical complications), there is a need for a reliable estimation procedure.

The most frequently studied thermodynamic property of an aqueous electrolyte in terms of the development of semi-empirical or semi-theoretical models has been the standard state entropy. Several notable studies have had varying degrees of success (POWELL and LATIMER, 1951; COBBLE, 1953a,b,c; LAIDLER, 1956; CONNICK and POWELL, 1953; MARCUS, 1986). Of present interest is the form of the equation used to represent the conventional standard state aqueous entropies. LAIDLER (1956, 1957) opposed any dependence of the estimated ΔS hydration (ignoring differences in standard states and the degeneracy of the ground state of certain species) on any combination of charge and radius besides z^2/r. All other workers found that other forms of charge and radius suited the available entropies at the time [for example POWELL and LATIMER (1951) suggested a dependence on $|z|/r_{eff}^2$, COBBLE (1953a,b,c) found the best dependence to be $|z|/r_{eff}$, and MORSS (private communication) found z_{eff}^2/r_{eff}]. There is no convincing support for the dependence predicted from electrostatic theories such as the Born equation (z^2/r). It is also apparent that the Born theory is inadequate in its ability to describe the change in entropy for hydration of gaseous ions. As will be shown, representations of standard

state entropies with all of the mentioned forms of the charge/radius term shows no appreciable differences except that a dependence on $|z|/r^2$ seems inferior to other representations. Finding the "best" representation of the standard state entropies of aqueous ions was deemed important because of the desire to extend these ideas to the much less investigated heat capacities of aqueous ions.

In 1964 Criss and Cobble (CRISS and COBBLE, 1964a,b) presented equations that yielded excellent correlations of the entropies and heat capacities for several different classes of inorganic electrolytes. These correlations have been widely used, but have been shown to be inadequate for certain aqueous species. The widespread use of these equations, and the relative importance that they have in relation to many fields including nuclear chemistry, geochemistry, and soil science has led to the present reinvestigation of such empirical relationships involving heat capacities of aqueous species.

19.2 The physical picture

The present approach is concerned with the representation of the standard state entropies and heat capacities of solutes in water. These aqueous species include monatomic and polyatomic ionic species, as well as neutral solutes. The standard state properties are assumed to be made up of the following contributions:

$$\bar{Y}^\circ + z\bar{Y}^{abs}_{H^+} - Y_{int} = Y_{elect} + Y_{phys} + Y_{struct}(\text{non} - \text{monatomics}) \qquad (19.1)$$

Here $\bar{Y}^\circ$ is the conventional ionic standard state property based on $\bar{Y}(H^+, \text{ aq}) \equiv 0$, $\bar{Y}^{abs}_{H^+}$ is the absolute property of hydrogen ion, Y_{int} is the "intrinsic" or solvent-free quantity that is equal to the value of the property in the gas-phase, Y_{elect} is the electrostatic contribution often approximated by the Born equation, Y_{phys} is a non-electrostatic contribution that can be thought of as the contribution that a brass ball would make in water, and Y_{struct} is a function of the structure and nature of polyatomic species (as discussed later). Equation 19.1 is written so that the left hand side represents a quantity proportional to the hydration entropy or heat capacity [it is not exactly equal to the hydration property because of the neglect of differences in the standard states of species in solution (hypothetical 1 molal) and in the gas phase (ideal gas at 1 bar pressure)].

Some of these quantities have rigorous theoretical significance (all are intended to have *some* theoretical basis). The quantity $\bar{Y}^{abs}_{H^+}$ has been estimated for both entropies and heat capacities by a variety of methods (CONWAY, 1978; ABRAHAM and MARCUS, 1986; TREMAINE *et al.*, 1981). This quantity is well defined for entropies and thus should not be used as a fit parameter. For heat capacities, however, uncertainties in this value are as much as ± 50 J $K^{-1}mol^{-1}$ and thus this term should not be constrained. Y_{elect} represents the "true" electrostatic contribution to standard state properties and not that approximated by the Born equation. It is thought that part of the success of several of the semi-empirical equations for the representation of standard state entropies as functions of z/r is due to the inadequacy of the Born equation (RASHIN and HONIG, 1985; ABE, 1986). Y_{phys} is used here to represent the contribution to the standard state properties due to the physical size of the species. This is most easily visualized in terms of partial molar volumes of aqueous solutes (HEPLER, 1957).

19.3 Selection of data

Table 19.1 summarizes all of the data used in calculations described in the next section.

All standard state heat capacities were taken from the critical compilation given in the preceding Chapter. Heat capacities for the gaseous monatomic ions were approximated by values for these same monatomic neutral atoms as listed in the NBS tables (WAGMAN *et al.*, 1982). Heat capacities for gaseous polyatomic ions were taken almost entirely from the calculated values of MARCUS and LOEWENSCHUSS (private communication) that are to be published. Some species that were not listed by these authors were estimated according to similarities with other ions.

Standard state entropies were taken from a variety of sources. The majority of values came from the NBS tables (WAGMAN *et al.*, 1982). Values for lanthanum, scandium, and chromium(VI) species were taken from the reviews of Hepler and co-workers (HEPLER and SINGH, 1976; TRAVERS *et al.*, 1976; DELLIEN *et al.*, 1976). Values for the rare earth elements were taken from SPEDDING *et al.* (1977), and values for most of the listed actinide elements were derived from MORSS (1986).

Table 19.1: Thermodynamic properties and other quantities selected for the present fits.

Species	$\bar{S}^\circ$ (J $K^{-1}mol^{-1}$)	S_{gas} (J $K^{-1}mol^{-1}$)	$\bar{C}_p^\circ$ (J $K^{-1}mol^{-1}$)	$C_{p,gas}$ (J $K^{-1}mol^{-1}$)	r_{IR} (Å)
Li^+	13.4	138.5	61.8	20.9	0.590
Na^+	59.0	153.6	42.5	20.9	1.020
K^+	102.5	160.2	12.7	20.9	1.510
Rb^+	121.5	164.0	-9.0	20.9	1.610
Cs^+	133.1	175.3	-23.7	20.9	1.780
Ag^+	72.7	172.8	36.0	20.9	1.150
Mg^{2+}	-138.1	148.5	-14.7	20.9	0.720
Ca^{2+}	-53.1	154.8	-25.0	20.9	1.120
Sr^{2+}	-32.6	164.0	-35.0	20.9	1.260
Ba^{2+}	9.6	171.1	-46.0	20.9	1.470
Mn^{2+}	-73.6	173.6	-10.0	20.9	0.830
Co^{2+}	-113.0	179.5	-29.0	20.9	0.745
Ni^{2+}	-128.9	177.0	-41.6	20.9	0.690
Cu^{2+}	-99.6	166.1	-20.0	20.9	0.730
Zn^{2+}	-112.1	161.1	-21.4	20.9	0.740
Cd^{2+}	-73.2	167.8	-6.0	20.9	0.950
Al^{3+}	-321.7	164.4	-119.3	21.3	0.535
Pb^{2+}	10.5	175.4	-55.0	20.8	1.290
Hg^{2+}	-32.2	175.0	-15.0	20.8	1.140
Fe^{2+}	-107.1	180.5	-25.0	25.7	0.780
Fe^{3+}	-315.9	180.5	-105.0	25.7	0.645
La^{3+}	-217.6	170.3	-137.0	20.9	1.160
Ce^{3+}	-205.0	191.8	-85.0	23.1	1.143
Pr^{3+}	-207.1	189.8	-137.0	22.8	1.126
Nd^{3+}	-206.3	189.4	-125.0	22.1	1.109
Sm^{3+}	-206.7	183.0	-119.0	30.3	1.079
Eu^{3+}	-215.5	188.8	-105.0	20.8	1.010
Gd^{3+}	-205.9	194.3	-97.0	27.5	1.000
Tb^{3+}	-226.0	203.6	-100.0	24.6	0.980
Dy^{3+}	-231.0	196.6	-90.0	20.7	0.970
Ho^{3+}	-226.8	195.6	-94.0	20.8	0.962
Er^{3+}	-244.3	195.6	-101.0	20.8	0.945
Tm^{3+}	-243.0	190.1	-94.0	20.8	0.994
Yb^{3+}	-238.0	173.1	-109.0	20.8	0.985
Lu^{3+}	-264.0	184.8	-103.0	20.9	0.919
Sc^{3+}	-255.0	174.8	-68.0	22.1	0.745
Y^{3+}	-251.0	179.5	-61.0	25.9	0.900
Tl^+	125.5	181.0			1.500

Table 19.1: continued.

Species	$\bar{S}^\circ$ (J $K^{-1}mol^{-1}$)	S_{gas} (J $K^{-1}mol^{-1}$)	$\bar{C}_p^\circ$ (J $K^{-1}mol^{-1}$)	$C_{p,gas}$ (J $K^{-1}mol^{-1}$)	r_{IR} (Å)
Tl^{3+}	-192.0	181.0			0.980
Th^{4+}	-422.6	190.1			0.940
Be^{2+}	-129.7	136.3			0.450
U^{3+}	-192.0	199.8			1.025
U^{4+}	-410.0	199.8			1.000
Pu^{3+}	-184.0	177.1			1.000
Pu^{4+}	-389.0	177.1			0.960
Np^{4+}	-389.0	197.6			0.980
Eu^{2+}	-8.0	188.8			1.170
Ga^{3+}	-331.0	169.1	-68.0	25.36	0.620
Cl^-	56.5	154.8	-126.9	21.8	1.810
Br^-	82.4	164.1	-131.0	20.8	1.960
I^-	111.3	169.7	-119.8	20.8	2.200
F^-	-13.8	146.3	-117.0	22.7	1.330
NH^{4+}	113.4	186.3	70.2	34.9	1.460
OH^-	-10.8	172.3	-140.0	29.1	1.370
SH^-	62.8	186.2	-94.0	29.1	1.840
NO_3^-	146.4	245.2	-71.8	44.7	2.920
ClO_3^-	162.3	264.3	-57.0	57.6	4.550
BrO_3^-	161.7	278.7	-91.5	60.3	4.700
IO_3^-	118.4	288.2	-32.0	62.0	4.940
ClO_4^-	182.0	263.0	-26.0	62.0	4.550
HSO_4^-	131.8	283.0	-19.0	70.9	3.050
MnO_4^-	191.2	277.8	-11.2	77.5	3.220
HSO_3^-	139.7	266.8	-10.0	53.0	3.150
HPO_4^{2-}	-33.5	283.0	-253.0	65.1	2.870
$H_2PO_4^-$	90.4	280.7	-34.0	65.0	2.870
CO_3^{2-}	-56.9	246.1	-300.5	44.4	2.910
SO_3^{2-}	-15.4	264.3	-263.0	52.6	2.960
SO_4^{2-}	20.1	263.6	-280.0	62.4	2.880
$S_2O_32^-$	67.0	291.1	-249.0	71.9	3.390
CrO_4^{2-}	50.2	281.4	-270.0	74.8	3.020
$HCrO_4^-$	184.1	302.0	2.0	74.6	3.020
MoO_4^{2-}	27.2	291.1	-207.8	77.0	3.350
PO_4^{3-}	-222.0	266.4	-495.0	65.4	2.870
HCO_3^-	91.2	257.9	-52.0	1.0	2.910
$Al(OH)_4^-$	102.9	293.0	96.2	109.3	3.310
$B(OH)_4^-$	102.5	270.5	-10.7	86.3	2.870

Table 19.1: continued.

Species	$\bar{S}^\circ$ (J $K^{-1}mol^{-1}$)	S_{gas} (J $K^{-1}mol^{-1}$)	$\bar{C}_p^\circ$ (J $K^{-1}mol^{-1}$)	$C_{p,gas}$ (J $K^{-1}mol^{-1}$)	r_{IR} (Å)
$Fe(CN)_6^{3-}$	270.3	491.6	-256.8	217.1	4.870
$Fe(CN)_6^{4-}$	95.0	469.8	-531.8	210.6	5.040
UO_2^{2+}	-97.5	260.4	44.4	49.0	1.820
Cl_3^-	138.9				3.620
ClO^-	42.0				3.170
ClO_2^-	101.3				4.550
Br_3^-	208.0				3.920
Bi^{3+}	-175.7	187.0			1.030
Ce^{4+}	-443.9	191.8			0.970
Ra^{2+}	54.0	176.5			1.480
CO_2	117.6	213.7	243.0	37.1	2.910
SO_2	159.5	248.2	195.0	39.8	3.130
NH_3	146.0	239.0	75.0	43.7	1.460
H_2S	121.0	205.8	178.5	34.2	1.840
He	54.4	126.1	145.0	20.8	1.310
Ne	66.1	146.3	165.0	20.8	1.390
Ar	59.4	154.8	190.0	20.8	1.700
Kr	61.5	164.1	210.0	20.8	1.800
Xe	65.7	169.7	255.0	20.8	2.050
$B(OH)_3$	162.3		107.4		2.870
S^{2-}	-14.6	152.1			1.840
CN^-	14.1	116.7			2.050
SCN^-	144.3	232.5			3.450
N_3^-	107.9	212.2			3.050
NO_2^-	123.0	236.3			2.920
BF_4^-	180.0	267.9			2.730
$AuCl_4^-$	266.9	363.8			4.300
$AuBr_4^-$	336.0	416.3			4.600
$Ag(CN)_2^-$	172.0	284.5			4.930
$Au(CN)_2^-$	172.0	284.5			4.630
$Hg(CN)_4^{2-}$	305.0	470.5			4.800
$Co(CN)_6^{3-}$	232.6	464.8			4.525

The value for ferrous ion was taken from Chapter 9 [derived from LARSON *et al.* (1968)]. Aqueous and gaseous standard state entropies for the species CN^- , SCN^-, N_3^-, NO_2^-, BF_4^-, $AuCl_4^-$, $AuBr_4^-$, $Ag(CN)_2^-$, $Au(CN)_2^-$, $Hg(CN)_4^{2-}$, and $Co(CN)_6^{3-}$ were taken from MARCUS (1986). Values for other entropies of the gaseous ions were taken from the NBS tables for monatomic ions and from LOEWENSCHUSS and MARCUS (1984) for polyatomic ions.

The listed radii were calculated from the "effective ionic radii" given by SHANNON (1976). Coordination numbers were generally taken to be equal to six except for those ions with known larger coordination numbers such as the lanthanide, actinide, and alkaline earth elements (SWADDLE and MAK, 1983; SPEDDING *et al.*, 1966; see also for example KRISTIANSSON *et al.*, 1988; LICHERI *et al.*, 1975; CAMINITI *et al.*, 1980; ALBRIGHT *et al.*, 1972) All of these values are listed in the following table.

19.4 Entropy correlations

19.4.1 Monatomic ions

The absolute entropy of H^+(aq) was assumed to be equal to -23.0 J $K^{-1}mol^{-1}$ (CONWAY, 1978) here and in all other calculations. The electrostatic contribution to standard state entropies as approximated by the Born equation can be represented by

$$\Delta S_{Born} = -\omega \frac{1}{\epsilon} \left(\frac{\partial \ln \epsilon}{\partial p} \right)_T \tag{19.2}$$

where ϵ is the static dielectric constant of water and ω for ionic species is given by

$$\omega = 6.9466 \times 10^5 \frac{z^2}{r_{eff}} \text{J Åmol}^{-1} - z\omega_{H^+}^{abs} \tag{19.3}$$

Radii normally used in the Born equation are denoted "effective" radii and are larger than crystallographic radii because they are meant to represent the "effective" radius of the ion in solution. This radius thus includes the tightly bound water dipoles, or more theoretically is related to the size of cavity required to accomodate the ion in solution (RASHIN and HONIG, 1985). In all calculations the additive component (normally a constant or a constant times charge) was varied to obtain best results.

Three functions were chosen in accord with expected theoretical and correlative evidence to make up for some of the inadequacies of the Born equation. The first

function was just another term in z^2/r, the next was that found to give the best results for fitting many entropies by COBBLE (1953) (z/r), and the last was that found by POWELL and LATIMER (1951) (z/r^2).

The term S_{int} is the entropy of the ion in the gas phase. Values of S_{int} are listed in Table 19.1. For monatomic ions, the gaseous entropies can be estimated by

$$S_{int} = S_{gas} \simeq c + \frac{3}{2} R \ln MW \tag{19.4}$$

ignoring ground state multiplicity, where R is the gas constant, and MW is the molecular weight of the ion. For fits of the monatomic ions, S_{int} values represented by this equation resulted in lower average deviations than did fits using S_{int} values taken equal to S_{gas} values that are listed in Table 19.1. The last term that is believed to make a major contribution to the hydration entropy is that represented by Y_{phys}. For partial molar volumes this term would be dependent on $(4/3)\pi r^3$. It is believed that the truly non-electrostatic contributions to these standard state entropies will also have a dependence on radius to the third power.

The resultant expression that can be derived assuming that further improvements can be made by using effective radii ($r_{eff} = r_{cryst} + \delta$, where δ may be different for cations and anions, and constant or a constant times charge)

$$\begin{aligned} \bar{Y}^\circ + z(-23.0) - 1.5R \ln MW \;\; = \;\; & a + bf(z,r) + \left(6.9466 \times 10^5 \frac{z^2}{r_{eff}} - \right. \\ & \left. 2.2554 \times 10^5\right) \Delta S_{Born} + c r_{eff}^3 \end{aligned} \tag{19.5}$$

Some of the reasons for past correlations employing different forms of $f(z,r)$ became apparent upon doing subsequent calculations. For $f(z,r) = z^2/r_{eff}$ the overall error in the fit was lowest. Functions of types $f(z,r) = z/r_{eff}$ and $f(z,r) = z/r_{eff}^2$ had marginally higher overall deviations. Fits with $f(z,r) = z^2/r_{eff}$ resulted in *even better* fits if the Born term was ignored thus putting all electrostatic contributions into z^2/r_{eff}. δ was found to be zero (within statistical significance) for anions. The final fit for monatomic ions had the form

$$\bar{Y}^\circ + z(-23.0) - 1.5R \ln MW = 80.11 - \frac{141.85 z^2}{r + \delta} + 5.731(r + \delta)^3 \tag{19.6}$$

where

$$\delta_{M^{z-}} = 0 \tag{19.7}$$

and

$$\delta_{M^{z+}} = 0.634z \tag{19.8}$$

The results of this fit are plotted in Figure 19.1. The average deviation that results from the fit is 12.2 J $K^{-1}mol^{-1}$ for 53 ions, significantly smaller than the average deviations reported by POWELL and LATIMER (1951) or by LAIDLER (1956) both that considered ions that presently give smaller deviations than some newly added ions. The present average deviation is comparable to the average deviation of 15.0 J $K^{-1}mol^{-1}$ obtained by a fit of a revised Powell-Latimer equation to nineteen cations by SCOTT and HUGUS (1957). The only ions that are realistically outside of expected uncertainties are Lu^{3+}(30), Tl^{3+}(30), Sc^{3+}(28), Be^{2+}(46), and Pu^{3+}(33 J $K^{-1}mol^{-1}$). All of these dicrepancies can be attributed to difficulties in the aqueous chemistry of these ions.

19.4.2 Entropies of all aqueous species

The very promising results presented above from the fit to standard state entropies of monatomic ions is now extended to polyatomic ions and a few selected neutral inorganic molecules. The term represented by S_{struct} arose from consideration of the heat capacities of neutral solutes containing terminal oxygen atoms. For example, the heat capacities of undissociated $MgSO_4$, HIO_3, and UO_2SO_4 are all negative (WOOLLEY and HEPLER, 1977; Chapter 12) as discussed in Chapter 12. The standard state heat capacities of CO_2 and SO_2, however, are large and positive. The present author has assumed that the negative component of heat capacities (and other properties such as entropies) is proportional to the amount of oxygen single bond character in a given ion or molecule. The following equation was proposed to represent this character

$$Y_{struct} = d\left(\frac{n_O}{2n_O - |z|}\right)^2 \tag{19.9}$$

Here n_O is the number of oxygen atoms in the species. Species that have close to a minus 1 charge on each terminal oxygen atom should have an associated large contribution from this term (highest weight = 1) whereas neutral molecules should have a smaller contribution (MO_2 species = 0.25). For ions that do not contain any terminal oxygen atoms [including species such as $M(OH)_3$] this term is assigned a value of zero.

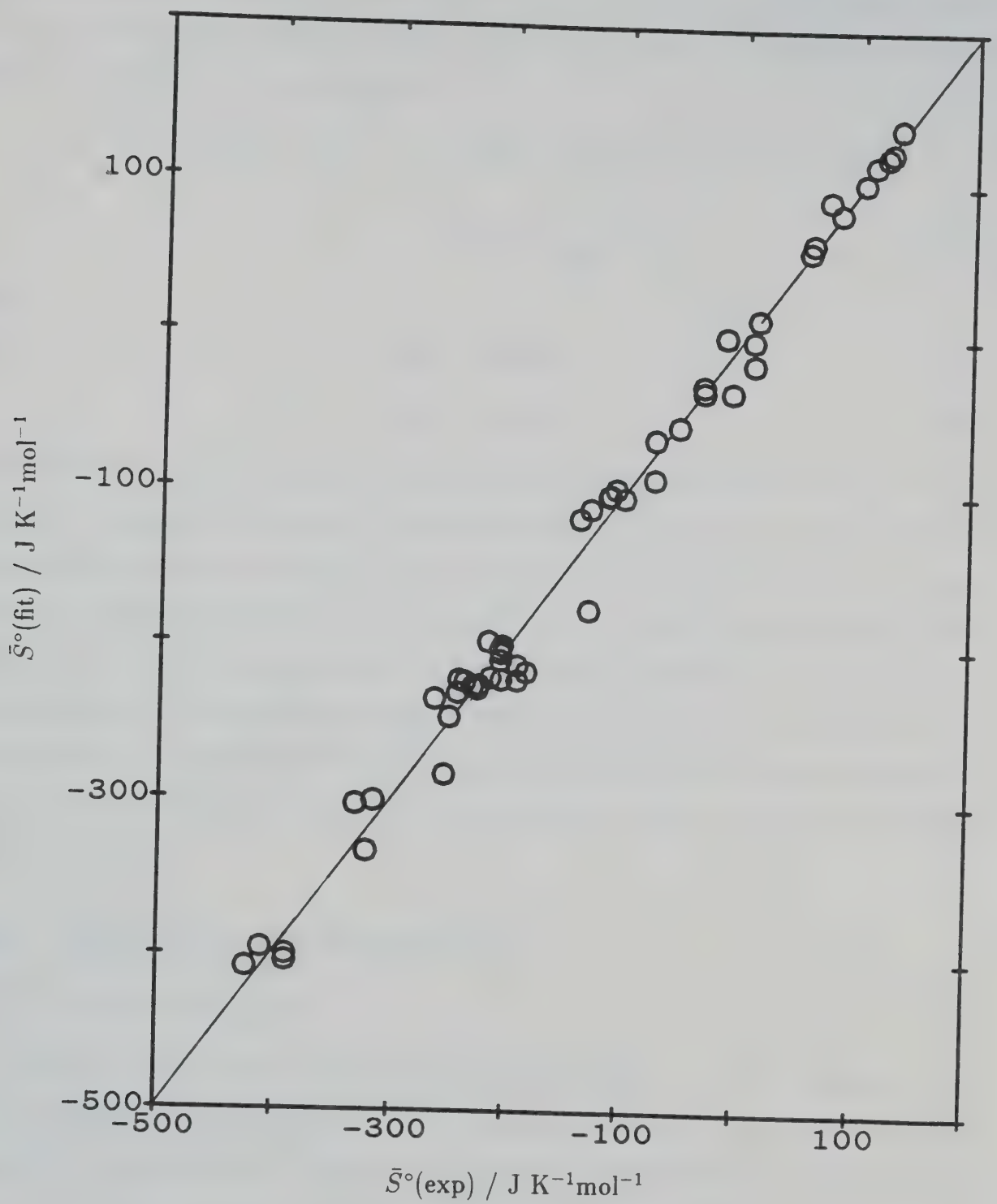

Figure 19.1: $\bar{S}°[M^z(aq)]$ (fit) plotted against $\bar{S}°(M^{z+})$ (experimental) according to eq. 19.6.

An equation of type 19.6 with the additional term given by eq. 19.9 was fitted to all appropriate data that are listed in Table 19.1. Here fits with different forms of $f = f(z, r)$ had quite different overall errors depending on the function. The lowest error was obtained for the equation:

$$\bar{S}^\circ + z(-23.0) - S_{gas} = -52.98 - \frac{95.91z^2}{r+\delta} + 0.06285(r+\delta)^3 - 128.49\left(\frac{n_O}{2n_O - |z|}\right)^2 \quad (19.10)$$

where

$$\delta_{M^{z-}} = 0.384|z| \quad (19.11)$$

$$\delta_{M^{z+}} = 0.355z \quad (19.12)$$

The results from this fit are plotted in Figure 19.2. The average deviation obtained using this expression fit to all of the data was 25.9 J $K^{-1}mol^{-1}$ about double the average deviation for monatomic ions. Largely, the species that have well known chemical handling problems are responsible for the observed higher average deviation. The correlation suggested by COBBLE (1953a) uses different $r + \delta$ values for several classes of ions (leading to more variable parameters than reported here). Because of the good agreement between the present scheme and the experimental data, this approach can now be extended to standard state heat capacities as described following.

19.5 Heat capacity correlations

19.5.1 Monatomic ions

Equations of the type given by eq. 19.6 were fitted to the heat capacity values for gaseous and aqueous species that are listed in Table 19.1. $C_{p,int}$ was taken to be equal to $C_{p,gas}$ in all fits. The Born component of the electrostatic term is given by:

$$\Delta C_{p,\,Born} = \omega T \frac{1}{\epsilon}\left[\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_p - \left(\frac{\partial \ln \epsilon}{\partial T}\right)_p^2\right] \quad (19.13)$$

An expression of type 19.5 was used to fit the standard state heat capacities of the monatomic ions. The same functions for $f(z, r)$ were chosen to see if similar insensitivities were present. Some fits were also performed using constrained values

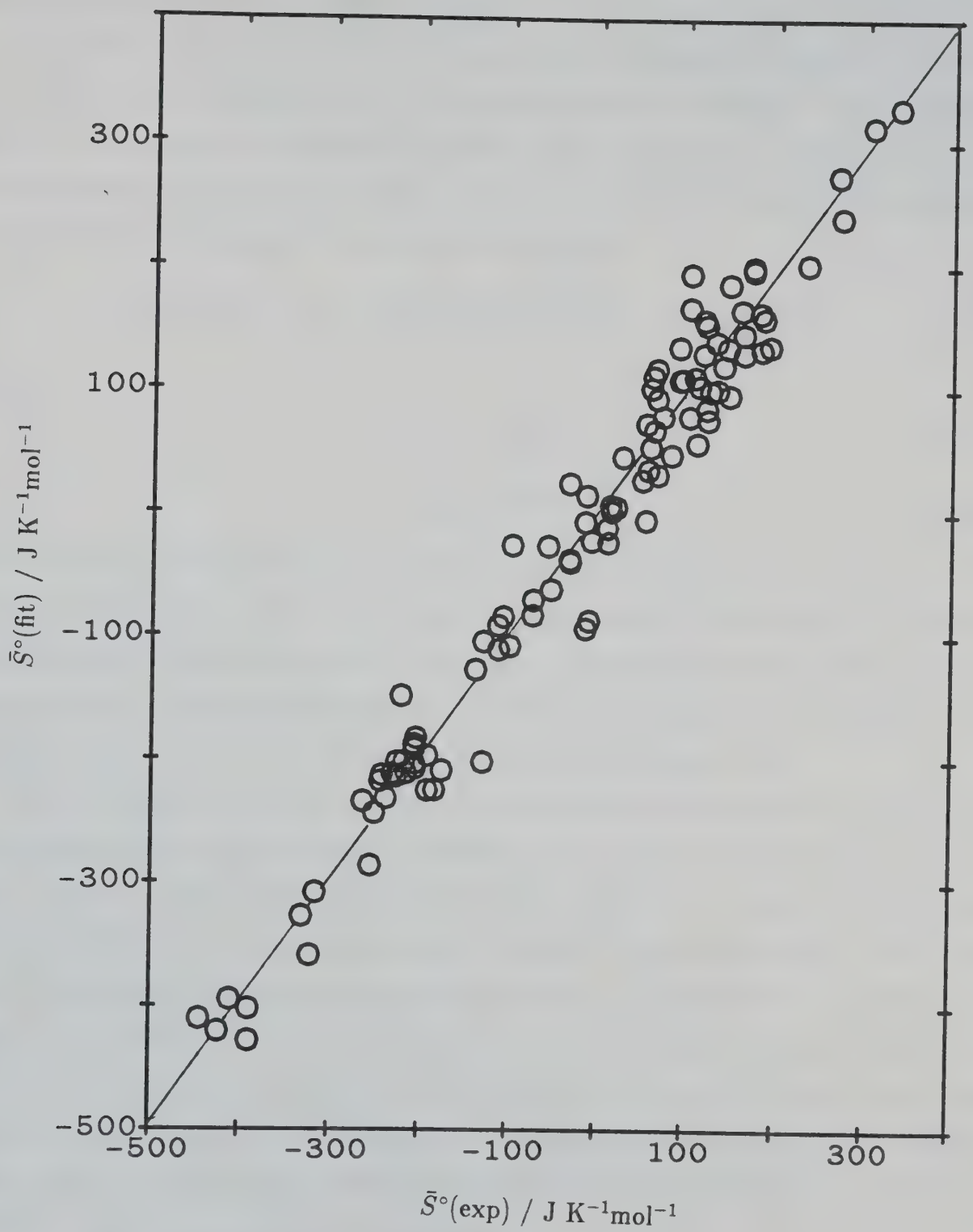

Figure 19.2: Fit versus experimental conventional entropies for aqueous species according to eq. 19.10.

of the absolute heat capacity [normally chosen to be -61 J $K^{-1}mol^{-1}$ consistent with the recommendations of CONWAY (1978)].

The value of the Born term was constrained to its theoretical value as listed by HELGESON and KIRKHAM (1974). Here for monatomic ions the "best" representation of the standard state heat capacities had a charge and radius dependence consistent with results from COBBLE (1953a,b,c) and KING (1959) for the entropies of ions. The final equation for monatomic ions was:

$$\bar{C}_p^\circ + z(-102.1) - C_{p,\,gas} = 264.9 - \frac{864.09z}{r+\delta} - 1.410(r+\delta)^3 \qquad (19.14)$$

with

$$\delta_{M^{z-}} = 2.127 \qquad (19.15)$$

$$\delta_{M^{z+}} = 3.880 \qquad (19.16)$$

that represented experimental data with an average deviation of less than 12 J K^{-1}-mol^{-1}. Incorporation of the Born term or a variable term of the type z^2/r resulted in substantially higher deviations. In contrast to entropies, the standard state heat capacities show significantly better results when the charge/radius function is represented by z/r. The results of this fit are displayed in Figure 19.3.

The *total* uncertainties for many of the ions used to generate this equation have substantially larger uncertainties than the reported average deviation (see Chapter 18). Deviations from other empirical equations such as that given by CRISS and COBBLE (1964b) are ***significantly*** higher than the present deviations. The fitted value of the absolute heat capacity of H^+(aq) (-102 ± 1 J $K^{-1}mol^{-1}$) is slightly more negative than other estimates (ABRAHAM and MARCUS, 1986). Results of fits to all of the species (those that have all required data) are preferred for evaluation of the absolute heat capacity of hydrogen ion. The equation cited above for monatomic ions should be used for these species and not the more general equation cited later.

19.5.2 Heat capacities of all species

Identical expressions were fitted to the whole data set (not just monatomic ions, as in eqs. 19.14-19.16) that is presented in Table 19.1. The $C_{p,\,struct}$ term is given by eq. 19.9. Marginal improvement was found in fitting all of the species if the constrained

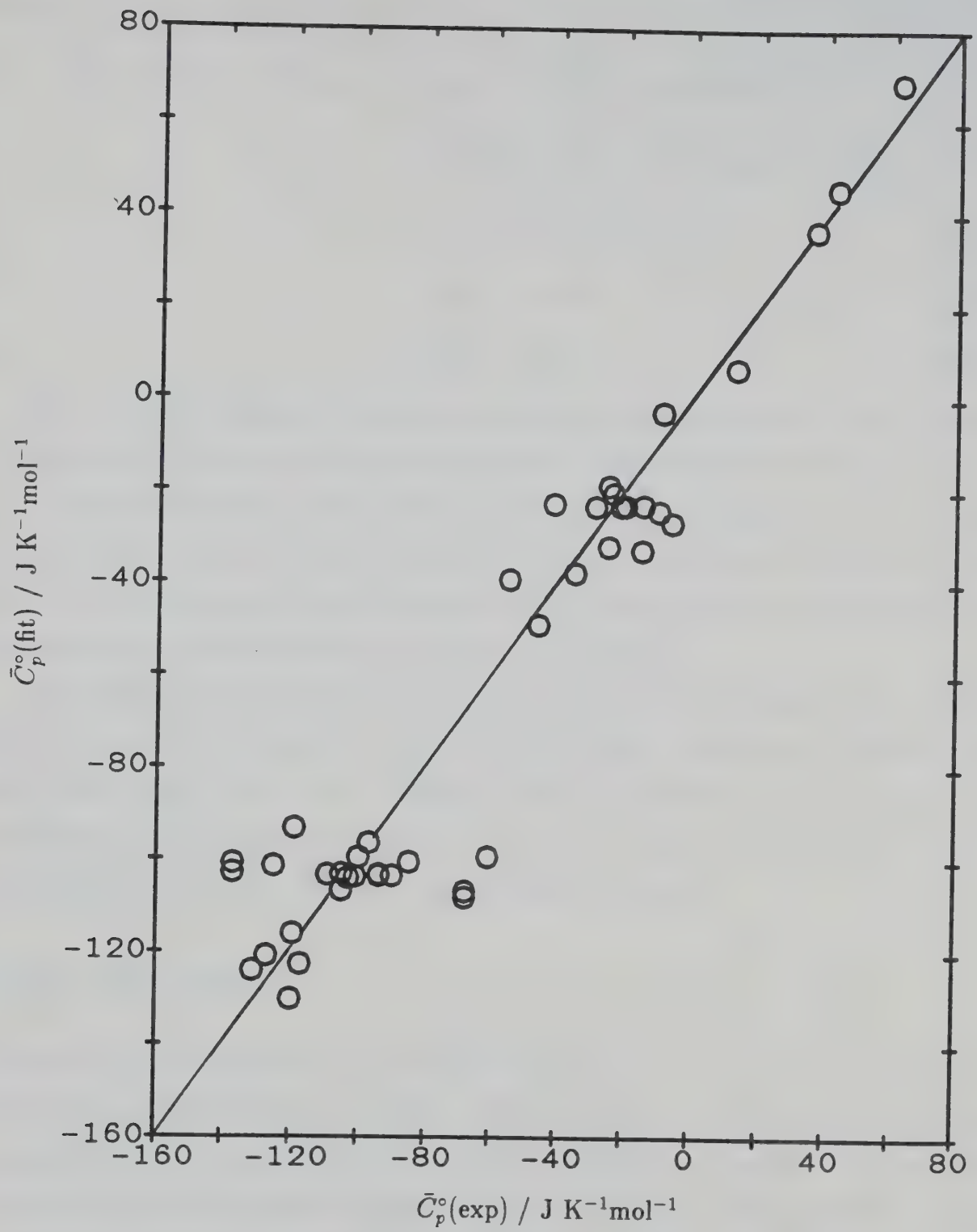

Figure 19.3: $\bar{C}_p^\circ[M^z(aq)]$ (fit) plotted against $\bar{C}_p^\circ(M^z(aq))$ (experimental) according to eq. 19.14.

$\Delta C_{p,\,Born}$ was included in the fits. The final equation for the heat capacities of all species was found to be

$$\bar{C}_p^\circ + z(-43.0) - C_{p,\,gas} = 144.8 - \frac{516.29z}{r+\delta} - 0.4852(r+\delta)^3 + 27.26\left(\frac{n_O}{2n_O - |z|}\right)^2 + \left(6.9466 \times 10^5 \frac{z^2}{r_{eff}} - 2.2554 \times 10^5\right) \Delta C_{p,\,Born} \quad (19.17)$$

$$\delta_{M^{z-}} = 1.035 \quad (19.18)$$

$$\delta_{M^{z+}} = 4.744 \quad (19.19)$$

The average difference between the calculated and experimental values that are presented in Table 19.1 and shown graphically in Figure 19.4 is about 21 J $K^{-1}mol^{-1}$. This average difference is not significantly larger than uncertainties in the experimental values. There are several ions that deviate significantly from the predicted curve. As can be judged from Figure 19.4, there are still minor shortcomings in the representation of heat capacities for polyatomic species.

The value derived for the absolute heat capacity of $H^+(aq)$ agrees with the best estimates presently available (-71 to +13 J $K^{-1}mol^{-1}$; ABRAHAM and MARCUS, 1986; TREMAINE *et al.*, 1981). Because of the consideration of neutral molecules, and ionic species ranging in charge from -3 to +3, the present value of -42 J $K^{-1}mol^{-1}$ is thought to be at least as reliable as the other estimates.

19.6 Discussion

The present equations for the entropies of monatomic ions show the smallest deviation of any scheme reported to date. Representations of entropies for polyatomic species are also reasonably good (not as good as the monatomics) considering that all species (cations, anions, neutrals) are represented by a single equation. Because of this simultaneous representation of neutral, cationic, anionic, monatomic, and polyatomic species, the present approach is believed to be more akin to theoretical improvements in the modeling of the hydration entropies of ions.

Of more importance here are the equations for the prediction of the standard state heat capacities of aqueous species. The two studies that can be compared with

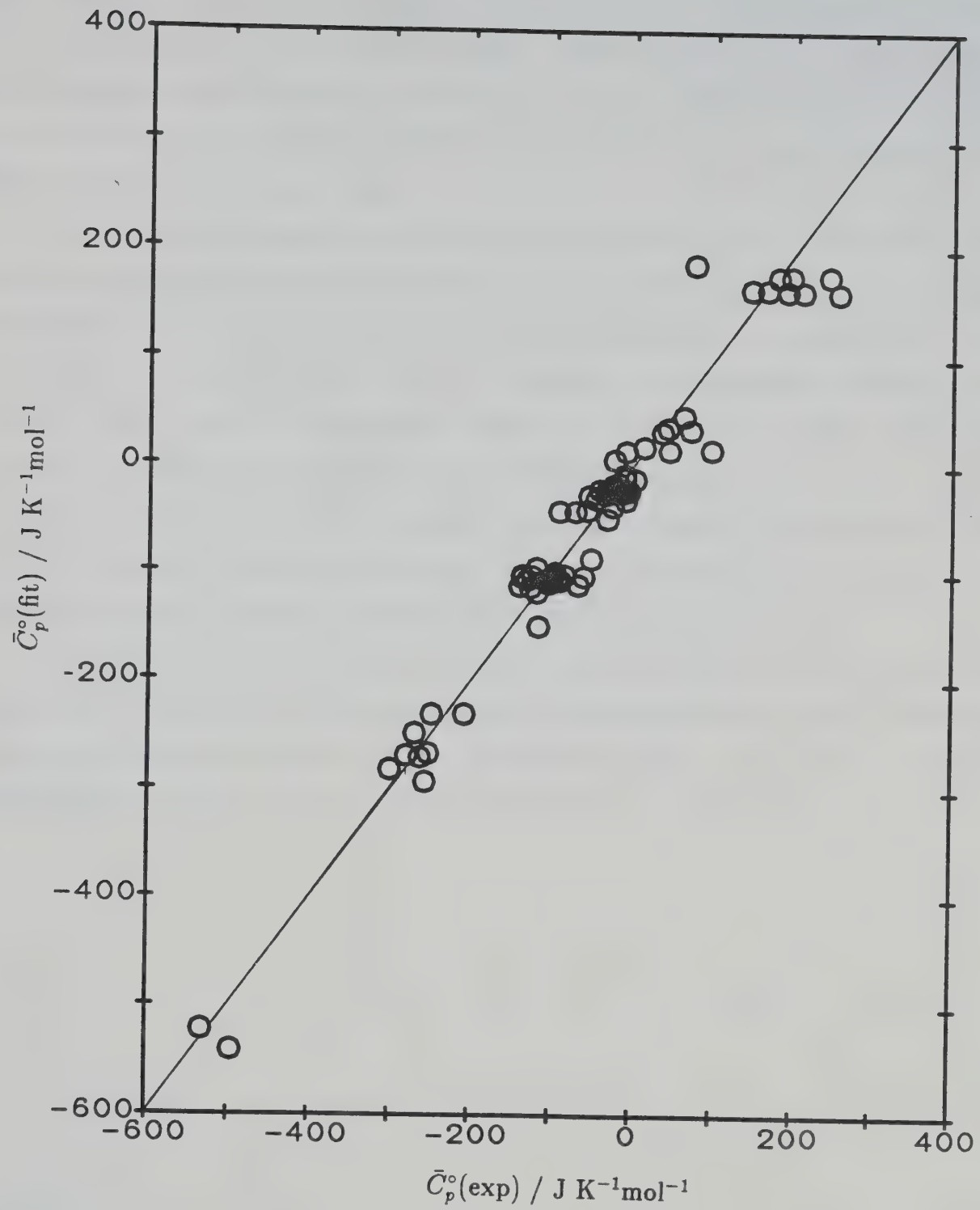

Figure 19.4: Fit and experimental conventional heat capacities for aqueous species according to eq. 19.17.

the present results are the Criss-Cobble entropy correspondence principle (CRISS and COBBLE, 1964a,b) and the recent correlation using a multi-layered electrostatic theory by ABRAHAM and MARCUS (1986). The predictions of the present scheme for monatomic ions (with fewer variable parameters) result in an average deviation smaller than that reported by ABRAHAM and MARCUS (1986) partly because of the difference in the data bases used.

The differences between the present approach and the results of CRISS and COBBLE are substantial (again mostly because of the limited data that the correlation was based on). For example, the Criss-Cobble scheme predicts a standard state heat capacity for $Al^{3+}(aq)$ of 16 J $K^{-1}mol^{-1}$ compared with the present prediction of -116 J $K^{-1}mol^{-1}$ and the experimental value of -119 J $K^{-1}mol^{-1}$. The Criss-Cobble scheme is, however, quite satisfactory for divalent metal ions as discussed in Chapter 3. The discrepancy here further supports the claim (Chapter 6) that the agreement with the standard state heat capacity of $Th^{4+}(aq)$ obtained by way of temperature dependent heats of solution is fortuitous (MORSS and MCCUE, 1976).

We have intentionally not discussed more theoretical implications of the present approach. This is due to planned expansions and a more theoretical analysis of equations similar to those used here. The present scheme is thought to be reliable and should be used until further improved equations are developed.

19.7 References

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Chapter 20

Concluding summary

It is apparent from the preceding Chapters that the data acquired in this study are of fundamental importance in calculations of classical thermodynamic quantities and as data that can be used to test and/or develop theoretical or semi-theoretical treatments of solute hydration.

The principal focus of the present work was to provide accurate thermodynamic data that can lead to physical chemical information regarding aqueous solutes. One particularly important area of investigation reported in several Chapters focussed on the quantitative assessment of "chemical relaxation" to total measured heat capacities of aqueous solutions containing partially dissociated solutes. The observed heat capacities of aqueous solutions containing partially dissociated solutes are higher than expected merely from equilibrium amounts of all species present in the solution. Due to the nature of a heat capacity determination (imposed temperature increment), the degree of dissociation of the solute changes (if there is a finite enthalpy change associated with the dissociation reaction) with temperature and thus changes during the course of the experimental measurement. Several treatments of this effect that have applicability in related areas were developed in the present work. The most complicated treatments assessed the contribution of "chemical relaxation" when more than one dissociation reaction was present and also in the important case when two or more reactions are coupled.

Another result of the present work has been the provision of data that can be used to describe the state of solutes in water. For example, several Chapters have reported thermodynamic data for several metal-ion complexation reactions with EDTA (ethylenediaminetetraacetic acid). These data have provided support for conclusions based on spectroscopic results regarding the nature of metal-chelate binding. Other

metal-ligand studies involved investigations of the thermodynamic properties associated with the formation of the predominantly inner-sphere uranyl sulphate complex. The negative conventional heat capacity for this species and other metal sulphates suggests strong solute-solvent interactions and volume and heat capacity functions approaching $-\infty$ near the critical point of water.

A large effort in the present work was directed toward classical calculations involving various measured and critically evaluated thermodynamic data. Because of the fundamental relationships of standard state heat capacities and volumes to Gibbs free energies and equilibrium constants, these data have been shown to be very useful for the prediction of temperature and pressure dependences of such equilibrium properties for a wide variety of reactions. These types of calculations (or more exactly the data used in these calculations) are important for describing the speciation in high temperature and pressure aqueous solutions that are useful in many applications. Various calculations have led to investigation of several mineral solubilities and also to a more general treatment of the thermodynamic properties associated with the hydrolysis of 3+ cations in aqueous solution. This latter treatment results in predicted mineral solubilities that agree with the best experimental data currently available to over 250°C. These results also suggest the use of these calculations for as yet uninvestigated high temperature mineral solubility reactions.

Finally, the relatively large number of measurements presented in the thesis naturally gave rise to an evaluation and compilation of the standard state heat capacities obtained by way of modern calorimetric measurements. These evaluations were found useful in investigations of the standard state entropies and heat capacities of aqueous solutes based on a semi-theoretical physical picture of these solutes in water. These latter calculations seem to be reliable for predicting standard state heat capacities and entropies for "missing" species that then can be used in calculations similar to those cited above.